Final thesis

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REDUCING HCl AND SO_2 EMISSIONS WITH DRY FLUE GAS CLEANING PROCESS –

HCl- JA SO_2-PÄÄSTÖJEN VÄHENTÄMINEN KUIVALLA SAVUKAASUN PUHDISTUSPROSESSILLA.

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ABSTRACT

Absorbent is injected into bubbling (BFB) or circulating (CFB) fluidized bed combustor to reduce emissions of sulphur. Injection can be made straight into the furnace (furnace injection) or after the boiler into the flue gas duct before particulate control device.

The purpose of this thesis was to find methods to improve dry flue gas cleaning process in bubbling fluidized bed combustor. Emissions were controlled with limestone injection into the furnace which was followed by a bag house filter.

The thesis consists of literature research and measurements in the test site. Flue gas emissions were studied in general in the research and possibilities to reduce emissions. The main focus was in dry flue gas cleaning process and its cleaning phases. Wet and semi-dry cleaning processes were covered briefly. Effects of process conditions on emissions were studied profoundly. The main focus was reducing of the acid gases, hydrogen chloride (HCl) and sulphur dioxide (SO_2).

The most important variables, which affected flue gas emissions, were discovered. Those were the effects of flue gas moisture (especially relative humidity), temperature and limestone feed to the process. Other variables were concentrations and contents of oxygen, nitrogen oxides and acid gases. Also the relation between hydrogen chloride and sulphur dioxide affected the composition of the flue gas.

Based on literature findings a test plan was made for site measurements. Many process conditions were attempted to cover in order that the effect of different process variables would be clarified.

Many of the sources in literature research were made in laboratories in simulated conditions. It was not possible to change every variable found in the research in full scale boiler circumstances. Other possible elements that could have an effect had to be taken into account in the analyses.

Variables that affected the emissions in this test run were found based on the measurements. The most important factors on reducing chloride and sulphur emissions were found to be relative humidity and temperature of the flue gas

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TIIVISTELMÄ

Kuivassa savukaasun puhdistusprosessissa kerrosleijukattilaan (BFB) tai kiertoleijukattilaan (CFB) syötetään absorbenttiä vähentämään rikkipäästöjä. Absorbentti voidaan syöttää suoraan kattilaan, jolloin puhutaan tulipesäinjektiosta tai kattilan jälkeen savukaasukanavaan ennen savukaasusuodatinta.

Työn tarkoituksena oli etsiä keinoja parantaa kuivaa savukaasun-puhdistusprosessia kerrosleijukattilassa. Päästöjen vähentämiseksi käytössä oli kalkkikivi-injektio tulipesään, jonka perässä oli letkusuodatin.

Työssä käytettiin kirjallisuusselvitystä ja käytännön mittauksia koelaitoksella. Kirjallisuusselvityksessä käytiin läpi ensin yleisesti eri savukaasupäästöjä ja niiden vähentämismahdollisuuksia. Päähuomio oli kuivassa prosessissa ja siihen kuuluvissa vaiheissa, mutta märkää ja puolikuivaa prosessia käytiin läpi myös pintapuolisesti. Tarkemmin tutkittiin eri prosessiolosuhteiden vaikutusta päästöjen vähentämiseen. Päästöt joiden vähentämiseen erityisesti keskityttiin, olivat vetykloridi (HCl) ja rikkidioksidi (SO_2).

Kirjallisuusselvityksessä löydettiin tärkeimmät muuttujat, jotka vaikuttavat päästöihin. Nämä olivat savukaasun kosteuden (varsinkin suhteellisen kosteuden), lämpötilan ja kalkinsyötön vaikutukset prosessiin. Muita tutkittavia olivat hapen, typen oksidien, happamien kaasujen konsentraatioiden ja määrien vaikutus sekä kloori-rikkisuhteen vaikutus.

Selvityksen perusteella laadittiin koeohjelma käytännön mittauksia varten. Koeohjelmassa yritettiin saada mahdollisimman erilaisia prosessiolosuhteita, jotta eri vaikuttajat tulisivat selkeämmin esille.

Monet kirjallisuusselvityksessä käytettyjen lähteiden tutkimukset olivat tehty simuloiduissa laboratorio-olosuhteissa. Täyden mittakaavan voimalaitosolosuhteissa ei kaikkia muuttujia voinut säädellä erikseen, joten niiden tulkinnassa on otettava huomioon muutkin mahdollisesti vaikuttavat tekijät. Jotta nämä mahdollisesti häiritsevät tekijät saataisiin rajattua pois, on tulosten analysoinnissa yritetty ottaa huomioon monia eri muuttujia ja eroavia tuloksia on jatkoselvitetty lisämuuttujilla.

Mittauksien perusteella löydettiin päästöihin tässä koesarjassa vaikuttavat tekijät. Tärkeimmiksi havainnoiksi nousivat savukaasun suhteellisen kosteuden ja lämpötilan vaikutus kloori- ja rikkipäästöihin.

PREFACE

This thesis was made for Metso Power during the spring of 2008 in cooperation with a Finnish power plant.

I would like to thank my instructor, Satu Lumme for her valuable guidance and help throughout this thesis and my advisors, Terhi Tallqvist, Risto Eteläaho and Henry Ylirönni for their advices, encouragement and effort. I would also like to thank my supervisor Torolf Öhman for his comments and knowledge throughout my studies.

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TABLE OF CONTENTS

ABSTRACT 2
TIIVISTELMÄ 3
PREFACE 4
UNITS, ABBREVIATIONS AND VOCABULARY 6
1. INTRODUCTION 7
2. FLUE GAS CLEANING 8
2.1 Flue gas emissions 8
3. Emission measurement 9
3.2 Absorbent 10
3.3 Self reduction 10
3.4 Flue gas cleaning process 10
3.5 General about wet and semi-dry process 16
4. IMPROVING THE DRY FLUE GAS CLEANING PROCESS 18
4.1 The effect of relative humidity 18
4.2 The effect of absorbent 20
4.3 The effect of HCl concentration to reduction 22
4.4 The effect of the relation between HCl and SO_2 23
4.5 The effect of O_2 on absorption process 25
4.6 The effect of NO_x on the absorption process 26
4.7 The effect of process conditions to furnace injection 27
4.8 Conclusions 38
5. MEASUREMENT EXECUTION 40
5.1 Test site 40
5.2 Experimental set-up 41
5.3 Flue gas analysers 43
5.4 Monitored emissions 43
6. MEASUREMENT RESULTS 45
6.1 The effect of flue gas moisture content 45
6.2 The effect of absorbent 51
6.3 The effect of temperature 54
6.4 The effect of concentration changes 55
6.5 The effect of the relation between HCl and SO_2 59
6.6 The effect of oxygen 59
6.7 The effect of NO_x 60
7. CONCLUSIONS 61
REFERENCES 64
APPENDIX 65

UNITS, ABBREVIATIONS AND VOCABULARY

BFB	bubbling fluidized bed
BHF	bag house filter
°C	degree Celsius
Ca	calcium
$CaCl_2$	calcium chloride
$CaCO_3$	calcium carbonate (limestone)
$CaMg(CO_3)_2$	dolomite
CaO	calcium oxide (burned lime)
$Ca(OH)_2$	calcium hydroxide (hydrated lime)
$CaSO_3$	calcium sulphite
$CaSO_4$	calcium sulphate
$CaSO_4*2H_2O$	gypsum
CFB	circulating fluidized bed
CO_2	carbon dioxide
d.s.	dry solid
ESP	electrostatic precipitator
FBC	fluidized bed combustion
FGD	flue gas desulphurisation
FTIR	Fourier transform infra red
HCl	hydrogen chloride
H_2O	water
H_2SO_4	sulphuric acid
i.e.	id est = that is
K	potassium
K_2SO_4	potassium sulphate
Mg	magnesium
$MgSO_4$	magnesium sulphate
MJ	mega joule (1MJ=1000 kJ=10^6 joule)
Na	sodium
NaCl	sodium chloride
$NaHCO_3$	sodium bicarbonate
NaOH	sodium hydroxide
NH3	hydrogen nitride (ammonia)
Nm^3	normal cubic meter (101,3 kPa, 273 K)
NO	nitrogen monoxide
NO_2	nitrogen dioxide
NO_x	nitrogen oxides
O_2	oxygen
PVC	polyvinyl chloride
RDF	refuse-derived fuel
REF	recovered fuel
RH	relative humidity
SEM	scanning electron microscope
SO_2	sulphur dioxide
SO_3	sulphur trioxide
vol-%	percentage by volume
w-%	percentage by weight

1. INTRODUCTION

In fluidized bed combustion system emissions of sulphur dioxide (SO_2) can be reduced by injecting calcium-based absorbent in the furnace. Absorbent which is typically used is limestone ($CaCO_3$).

In the furnace, $CaCO_3$ first calcines forming calcium oxide (CaO). After this CaO reacts with SO_2 and forms calcium sulphate ($CaSO_4$). $CaSO_4$ and exits the furnace together with bed material and fly ash.

Final SO_2 levels attained in the stack emissions, depend on the combustion circumstances, such as temperature and oxygen level in the furnace, sulphur content of the fuel, as well as moisture of the flue gas and absorbent used (amount and quality).

Hydrogen chloride (HCl) as well as sulphur dioxide emissions can be reduced by injecting absorbent into flue gas duct after the furnace. Absorbent typically used is hydrated lime $Ca(OH)_2$. Some reduction occurs in the duct but the mostly the reduction happens in the bag house filter after the duct. Absorbent forms a thick layer on the surface of the bag where the reduction occurs.

The thesis consists of literature research and analyses of measurements. The purpose of the literature research was to find out how different process parameters affect the cleaning process. Based on those findings, tests were planned.

The tests were executed in the beginning of March in a Finnish power boiler. The purpose of the test was to study the effect of different process parameters on flue gas emissions in a dry flue gas cleaning process. The main components that were examined were HCl and SO_2. The results were compared with the literature research findings.

The goal in measurement campaign was to find the right process conditions to maximise the reduction of sulphur dioxide and hydrogen chloride. Absorbent used in the measurements was $CaCO_3$. It was injected straight into the furnace.

2. FLUE GAS CLEANING

2.1 Flue gas emissions

2.1.1 Hydrogen chloride (HCl)

Most bio fuels and different refuse-derived fuels commonly contain 0.01-1 % d.s. chlorine (dry, solid). It often transforms into HCl during combustion. The biggest source of non organic chlorides is recovered fuel. Organic chlorides are mostly from plastics. Especially PVC is a big source of chloride. In the co-combustion of refuse-derived fuels (RDF) and more convential fuels such as coal or peat, both HCl and SO_2 co-exist in the flue gases (Table 1) [3].

Table 1: Typical fuel chloride contents

Fuel	Chloride content w- %
Spruce bark	0,02
Primary and secondary sludge	0,15
RDF	0,89
Peat	0,03
Bituminous coal	0,09
Petroleum coke	0,04

2.1.2 Sulphur dioxide (SO_2)

Sulphur is combined in fossil fuels in the elementary stage. Most of the sulphur in fuels oxidizes to sulphur dioxide (SO_2), a part of it oxidizes to sulphur trioxide (SO_3). Big sources of sulphur are coal and fuel oil. Sulphur content in bio fuels is so low that it does not usually form the need to clean it from flue gases (Table 2) [8].

Table 2: Typical fuel sulphur contents

Fuel	Sulphur content w- %
Heavy fuel oil	2,70
Light fuel oil	0,25
Spruce bark	0,03
Primary and secondary sludge	0,26
RDF	0,28
Peat	0,21
Bituminous coal	1,40
Petroleum coke	7,35

3. EMISSION MEASUREMENT

Flue gas emissions are measured constantly with different methods. One of the methods is a FTIR spectrometer (Fourier Transform Infra Red Spectrometer) (Figure 1).

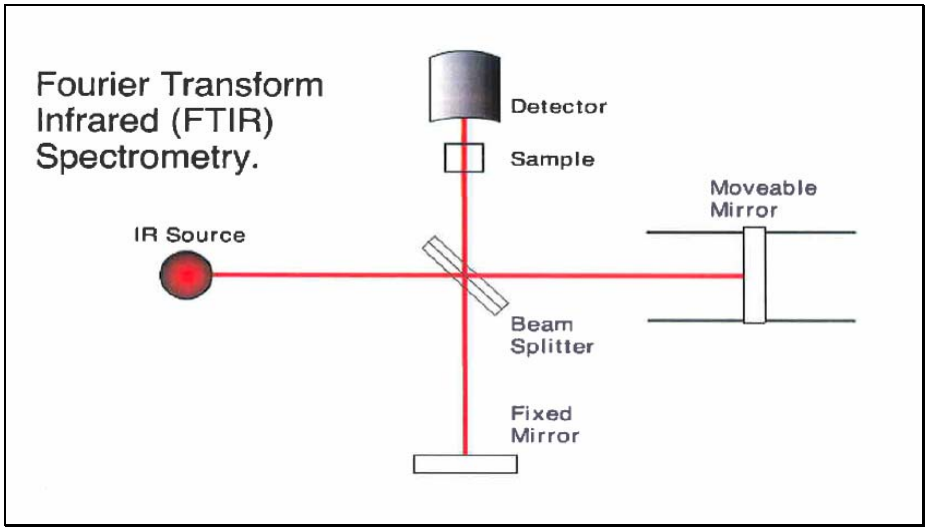

Figure 1: Fourier Transform Infra Red Spectrometer [12].

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation or other type of radiation [13].

It can be applied to a variety of types of spectroscopy including optical spectroscopy, infrared spectroscopy (IR), nuclear magnetic resonance, mass spectrometry and electron spin resonance spectroscopy [13].

There are several methods for measuring the temporal coherence of the light, including the continuous wave Michelson or Fourier transform spectrometer and the pulsed Fourier transform spectrograph (which is more sensitive and has a much shorter sampling time than conventional spectroscopic techniques, but is only applicable in a laboratory environment) [13].

3.2 Absorbent

The main purpose for using absorbent is its neutralising effect.
Often different kinds of limes are used: limestone ($CaCO_3$), dolomite $CaMg(CO_3)_2$, hydrated lime ($Ca(OH)_2$, burned lime (CaO) and pre-treated hydrated lime. An alternative absorbent is i.e. sodium bicarbonate ($NaHCO_3$) (Table 3). Sodium bicarbonate has to be grinded before use.

Table 3: Different absorbent bulk densities, prices and injection locations.

	Bulk density (kg/m^3)	Price (€/ton)	Use
Limestone	1300-1500	30-60	in the furnace
Dolomite	1400-1500	10-30	in the furnace
Burned lime	900-1200	95-125	after furnace
Hydrated lime	400-640	100-130	after furnace
Pre-treated hydrated lime	300-400	225-250	after furnace
Sodium bicarbonate	800-1200	200-240	after furnace

3.3 Self reduction

Self reduction can be significant when ash contains alkali compounds. All alkali metals i.e. Ca, Mg, Na and K can act as an absorbent and bind chloride and sulphur emissions. It means that HCl and SO_2 emissions reduce unassisted. Salts formed in process i.e. $CaSO_4$, $CaCl_2$, $MgSO_4$, NaCl, K_2SO_4 exit the boiler with bottom and fly ashes. Gaseous chloride and sulphur compounds separate from flue gas in the bag house filter [1].

3.4 Flue gas cleaning process

Main process types in flue gas cleaning are wet, semi-dry and dry process. Main focus in this research is dry flue gas cleaning process after the furnace with injection in the flue gas duct.

There are two possible places where absorbent can be injected (Figure 2): direct into the furnace (furnace injection) or injection in the flue gas duct. One of the methods does not exclude the other. There are some parameters in Figure 3, which have an effect on the selection of flue gas cleaning method. There is no simple solution in choosing which method to use; it has to be decided case by case.

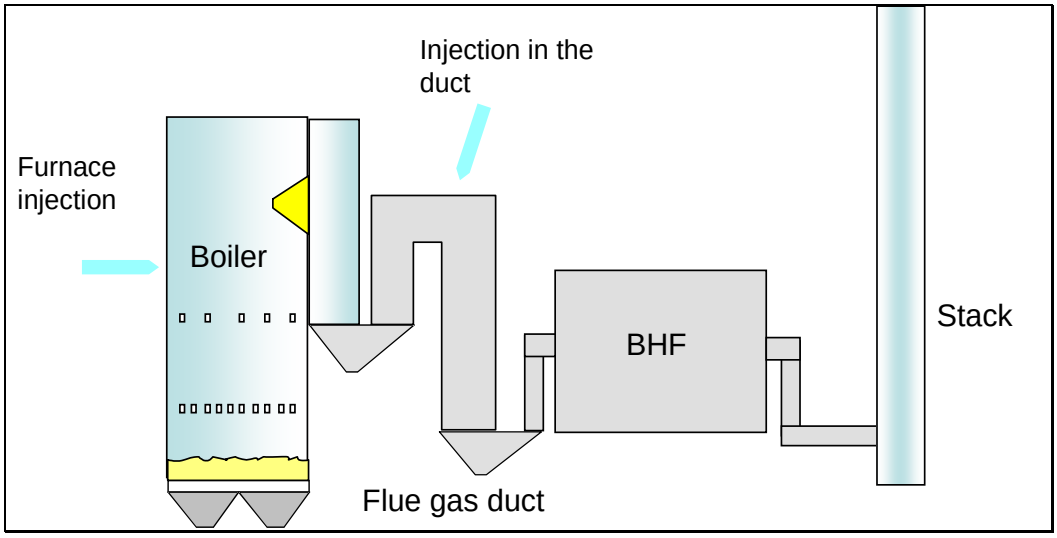

Figure 2: Dry flue gas cleaning process, furnace injection or injection in the flue gas duct [10].

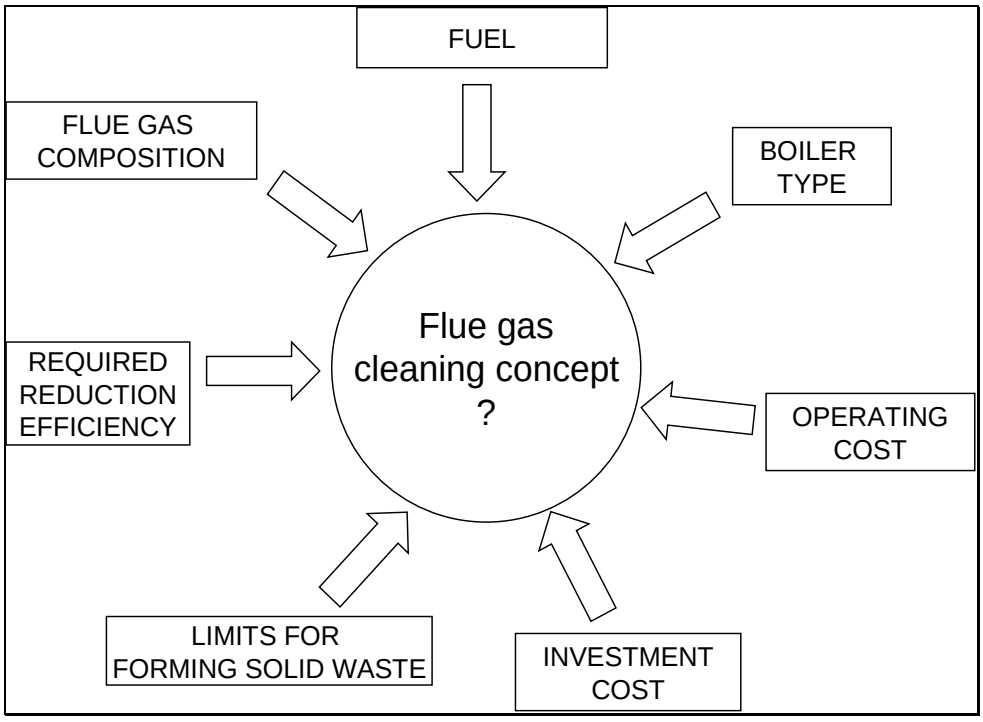

Figure 3: Parameters, which affect the selection of flue gas cleaning concept (furnace injection, injection in the flue gas duct or both).

Different flue gas cleaning methods were compared in a research by Holzman and Atkins in 1988 (used as reference in a study by Chrisholm and Rochelle 1999) The advantages of a dry absorbent injection after the furnace are the absence of wastewater, corrosion or steam plume problems (wet scrubbing), the absence of nozzle plugging (spray dryer absorption), greater absorbent utilization (furnace injection), its relative simplicity, and easy retrofitting according to the research [4].

3.4.1 Furnace injection

Ca-based absorbents are commonly added to bubbling and circulating fluidized bed combustors to control SO_2 emissions. It is made by furnace injection (Figure 4). Absorbent is injected straight into the furnace in powder form. With the right temperature and good contact with the absorbent sulphur can be absorbed. Absorbent which is usually used is limestone.

Porous limestone is a good absorbent for binding sulphur. It maintains it's porosity in fluidized bed temperatures. Finer limestone powder's advantages are its BET area and better sulphur binding capability. An adequate residence time is needed to reach good cleaning efficiency. Limestone calcines into burned lime in combustor temperatures according to following reaction.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \textbf{(Equation 1)}$$

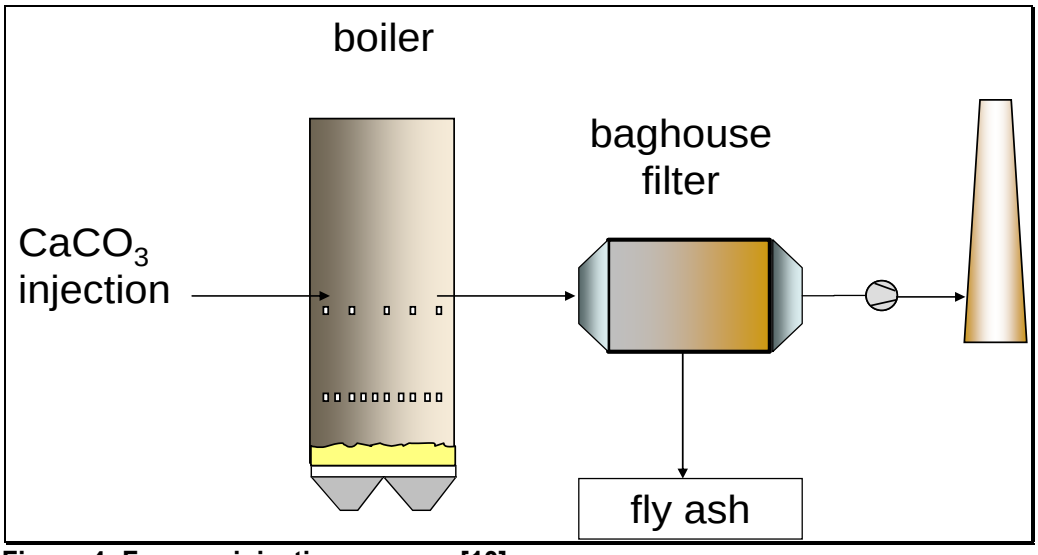

Figure 4: Furnace injection process [10].

The chemistry involved has been widely investigated over the past 30 years, but the mechanism of the sulphation process is not yet fully understood. A common understanding has been for instance, that under oxidising conditions, a product layer is formed on the absorbing particles and blocks the absorbent before complete conversion has occurred.

According to Anthony and Granatstein, however, there is new experimental evidence to suggest that with long sulphation times the

sulphation reaction could reach high conversions (study by Partanen et al. 2005) [3].

Less attention has been paid to the chlorination of limestone with HCl. Chlorination studies has been carried out mostly in the temperature range 200-650°C [6].

Reactions with CaO with HCl and SO_2 are the following.

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \quad \textbf{(Equation 2)}$$

$$CaO + SO_2 + ½O_2 \rightarrow CaSO_4 \quad \textbf{(Equation 3)}$$

With low concentration of independent HCl in the gas, the reaction with CaO slows down to such an extent that to get complete conversion would take a very long time. According to research by Lawrence and Bu, it is possible that (in the absence of other important combustion products such as SO_2) limestone would capture some HCl. However, this effect will be small because of the presence of significant amounts of moisture and the relatively slow conversion of the solid [7].

3.4.2 Flue gas cleaning with BHF

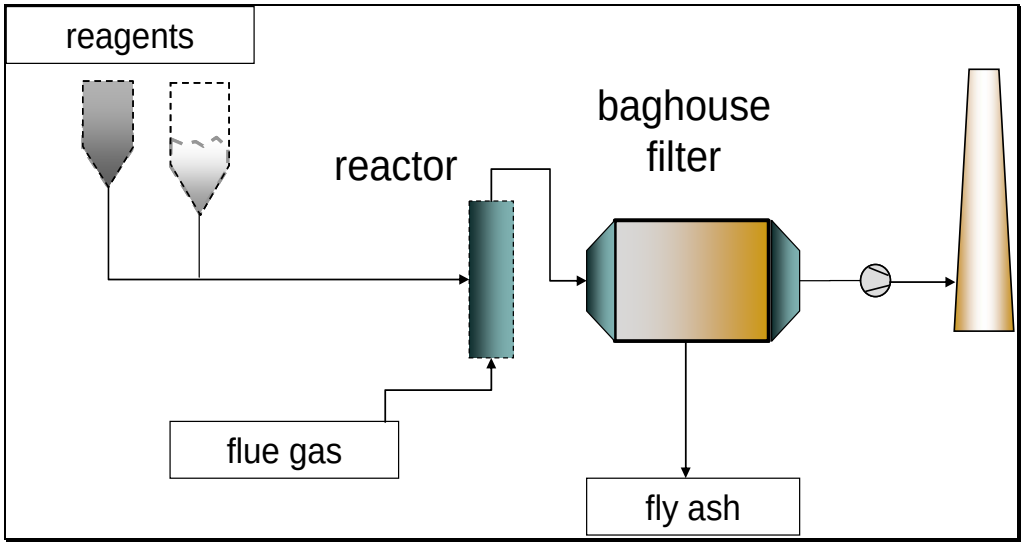

Figure 5: Dry flue gas cleaning process with a bag house filter [10].

If the boiler has a bag house filter for particulate control, one strategy is to inject a dry, alkaline sorbent into the flue gas to bind HCl and SO_2 (Figure 5). Flue gas temperature is usually ~150ºC after the furnace. Flue gas can be humidified and its temperature lowered before absorbent injection.

It can be made with moisturising phase i.e. a conditioning tower or a quench (Figure 6). Its function is to increase relative humidity. The function of a bag house filter is to remove pollutants from the flue gas stream in a controlled manner. Particles in the flue gas deposit on the external surface of the filter bags. In order to reduce acid gases (SO_2 and HCl) absorbent is added upstream of the filter [10].

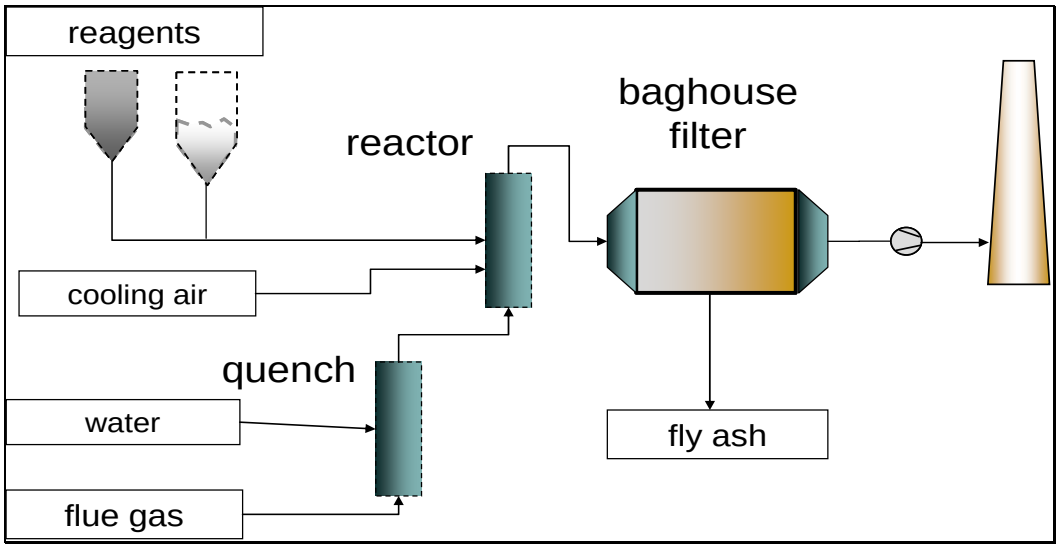

Figure 6: Dry flue gas cleaning process with a quench and a bag house filter [10].

In a bag house filter system absorbent is continually added. Absorbent contacts the bag and forms a thick layer on the external surface. The cake is cleaned from the bags according to the bag's cleaning cycle. It is the period between cleanings of the bag. Bag house filters are generally cleaned by a reversed air stream, by a pulse jet (Figure 7), or simply by shaking [4].

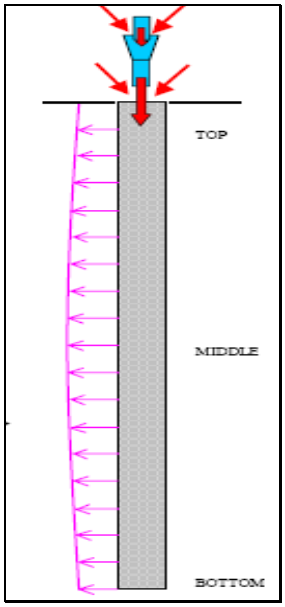

Figure 7: Pulse jet cleaning system [10].

Absorbents used are usually hydrated lime or sodium bicarbonate. To minimise the amount of heavy metals, dioxins and furans a small amount of activated carbon can also be injected. Some acid gas absorption will take place in the duct. However, most will occur on the surface of the BHF.

In the absorbing process gaseous HCl and SO_2 react with the absorbent. The reactions that happen in the process are the following.

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 * ½H_2O + ½H_2O \quad \textbf{(Equation 4)}$$

$$CaSO_3 + ½O_2 \rightarrow CaSO_4 \quad \textbf{(Equation 5)}$$

$$Ca(OH)_2 + 2HCl(g) \rightarrow CaCl_2 + 2H_2O(g) \quad \textbf{(Equation 6)}$$

Excess use of calcium causes following reaction instead of reaction (6).

$$Ca(OH)_2 + HCl(g) \rightarrow CaOHCl + H_2O \quad \textbf{(Equation 7)}$$

Presence of HCl affects the reaction with SO_2. CaOHCl formed in reaction (7) reacts with SO_2 in following way.

$$CaOHCl + SO_2 + ½H_2O \rightarrow CaSO_3 * ½H_2O + HCl \quad \textbf{(Equation 8)}$$

Formed HCl reacts further building more CaOHCl which binds more SO_2. This chain reaction continues until calcium content is reduced to minimum and reaction (6) occurs [1].

3.5 General about wet and semi-dry process

3.5.1 Wet process

Wet flue gas cleaning products are different kinds of scrubbers. Scrubber cleaning is performed with scrubbing the flue gas with washing solution. Washing solution used for SO_2 and HCl removal contains sodium hydroxide, hydrated lime or limestone (Figure 8). These kinds of scrubbers are used also after BHF in flue gas cleaning i.e. for NH_3 removal.

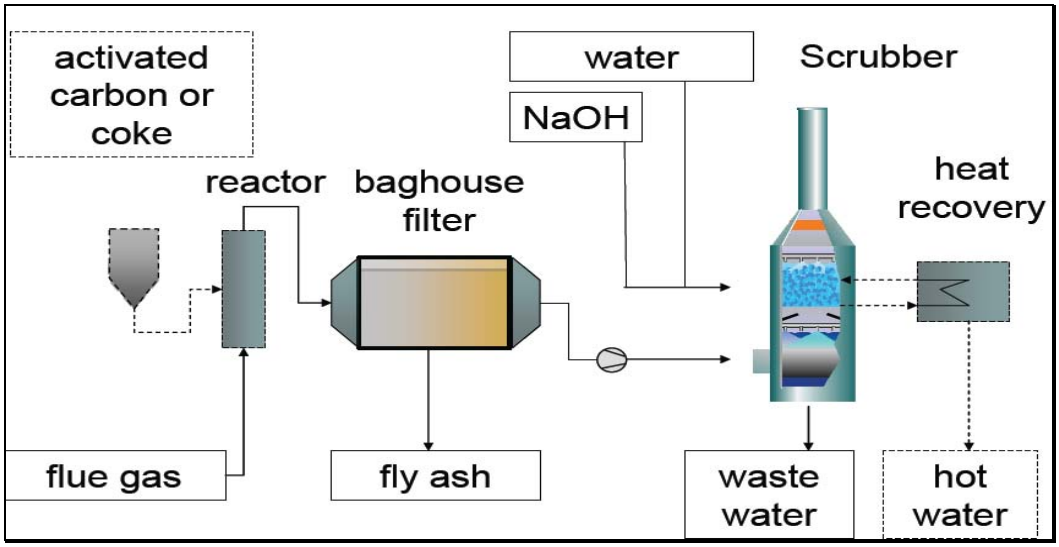

Figure 8: NaOH scrubber [10].

In wet limestone absorber the flue gas is brought to contact with alkaline solution in an absorber tower (Figure 9). Absorbent is added as limestone powder. The end product formed in process is gypsum ($CaSO_4$*$2H_2O$), which is separated from the solution by filtration. The formed gypsum can be used as raw material in different kinds of processes. Exhaust gas is led to mist eliminator before stack. Particulates are removed from the flue gas with electrostatic precipitator (ESP).

ESP's function is to remove particles from the flue gas stream, the same as bag house filter's. Electrostatic precipitator generates an electrostatic field across the path of particulate matter in the air stream. The particles become negatively charged and migrate towards positively charged collection plates. The collection plates are rapped or vibrated periodically, dislodging the material so that it falls into collection hoppers below [15].

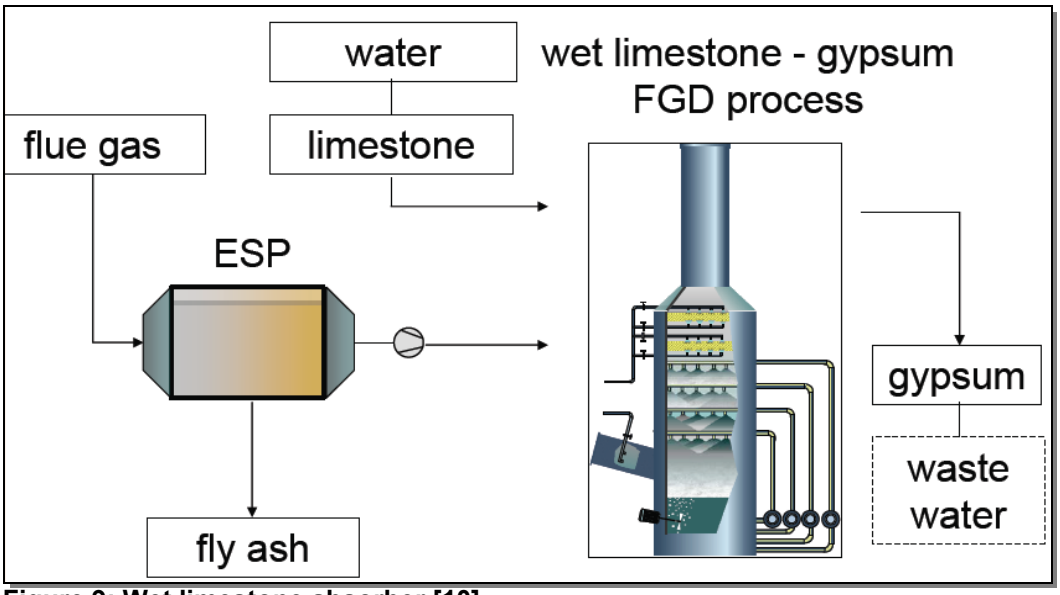

Figure 9: Wet limestone absorber [10].

3.5.2 Semi-dry process

Spray dry scrubbing is a commonly used method in semi-dry flue gas emission reduction after the furnace. A fine spray of lime slurry is dispersed concurrently into the flue gas stream. The acid gas components are absorbed in the droplets and react with the hydrated lime forming salts according to the reactions (4, 5 and 6). At the same time the water evaporates from the droplets and a dry, powdery product results. This is usually separated from the cleaned flue gas with a bag house filter or electric precipitator [5].

The separated product consists of the reaction products and unreacted absorbent. To obtain high absorption efficiency, an excess use of absorbent is required. Consequently the conversion is incomplete. Absorbents used commonly are hydrated lime ($Ca(OH)_2$) or burned lime (CaO) [5]. Hydrated lime is formed by hydration of burned lime according to the following reaction.

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad \textbf{(Equation 9)}$$

4. IMPROVING THE DRY FLUE GAS CLEANING PROCESS

Laws and directives concerning flue gas emissions have been tightened and it makes the process optimisation more important. There are many process conditions that affect the dry flue gas cleaning process. Emissions can be reduced in right process circumstances and because of efficient absorbent.
Better utilization of absorbent results in reduced use of absorbent. Reduced absorbent use and more efficient absorbents lead in reduced costs.

Process which effects are researched in this chapter is dry flue gas cleaning process with absorbent injection after the furnace in the flue gas duct (4.1-4.6 and 4.8). The conditions which affect furnace injection are examined briefly in chapter 4.7.

4.1 The effect of relative humidity

Relative humidity is an important parameter in process efficiency. With lower flue gas temperature high relative humidity can be achieved and a high cleaning rate. RH is a per cent value, which indicates the maximum amount of water that flue gas can contain before condensation. It is based on three parameters, which are flue gases water content, temperature and pressure (no effect in normal pressure situations). Lower temperatures mean that water content is lower. With constant water content relative humidity rises when temperature lowers. Higher RH should in theory make lime more effective. RH can be calculated with the following equations [13, 14]. Constants A-E are in the appendix (Table 6).

$$RH = \frac{x_{(H_2O)} * p_{(H_2O)}}{p'_{(H_2O)}} * 100\% \quad \textbf{(Equation 10)}$$

$$\log_{10} p'_{(H_2O)} = A + \frac{B}{T} + C * \log_{10} T + DT + ET^2 + 2{,}12490 \quad \textbf{(Equation 11)}$$

$x_{(H2O)}$= absolute moisture of water

$p_{(H2O)}$= partial pressure of the water vapour

$p'_{(H2O)}$= saturated vapour pressure in water

High RH can also produce problems by causing corrosion on the surface of heat exchanger. Sulphur and chlorine react with water forming sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) which are strongly corrosive. Minimum temperature has to be set (~125-140 ºC). With dryer flue gases the limit is little lower (~110-120 ºC) [1].

4.1.1 Independent absorption of HCl and SO_2

Absorption of HCl is enhanced at low temperature, primarily by an increase in RH. Absorption of HCl is found to be sensitive to relative humidity. With an increase in RH, HCl removal and amount of HCl combined with absorbent increases (HCl/Ca^{2+}-ratio). This ratio is the relation between moles of HCl and 1 mole of Ca. Increased reactivity of acid gases with increasing RH has been seen throughout the literature (i.e. in the Värmeforsk report [1].

As with HCl, the reactivity of SO_2 alone with absorbent increased with increasing relative humidity. Unlike HCl, decreasing SO_2 concentration increased the fraction of SO_2 removal [4].

Most of the experiments performed with HCl and SO_2 are conducted at high relative humidity because at lower RH, the reactivity of SO_2 is too low to observe trends with acceptable precision.

4.2 The effect of absorbent

Absorbents efficiency depends on its specific surface (BET area) and pore volume. Bigger BET area gives higher cleaning capacity. Pore volume is though more important factor. Certain amount of fly ash improves cleaning capacity by improving diffusion of HCl and SO_2. Density of absorbent affects only the absorbent volume.

Lime particle size has also got an effect on chemical reactions. Smaller particle size improves mixing of absorbent and flue gas. A bigger amount of injection points has also got good effects on mixing. Mixing helps absorption cake to spread in the filter surface improving efficiency [1].

One of the key operational conditions that impact the performance projections is the absorbent feed ratio. It is the number of moles of absorbent fed to the system divided by the number of moles needed to remove all the acid gas, assuming 100% utilization of the solids by simple acid-base reactions. For example, if 1 mol each of SO_2 and HCl entered, an absorbent feed ratio of 2 meant 3 mol (2*(1 mol+0,5 mol)) absorbent was fed into the duct.

The second important operational variable in a bag house filter system is the cleaning cycle. More effective use of absorbent can be achieved in theory by lengthen the residence time in filter. Longer cleaning cycle of filter causes thicker absorption cake and longer residence time. Removal of the bag is lowest immediately after being cleaned [1, 4].

4.2.1 Independent absorption of HCl

In the chlorination studies, high absorbent feed ratio causes low utilisation of the absorbent and almost 0 % penetration through the bag house filter occurs. As the absorbent feed ratio decreases, the utilization increases. But when the feed ratio is low, the absorbent must be utilized as much as possible and almost 100 % HCl penetration is predicted. Figure 10 projects that to reduce HCl penetration to 10 %, slightly more than half the absorbent will be utilized [4].

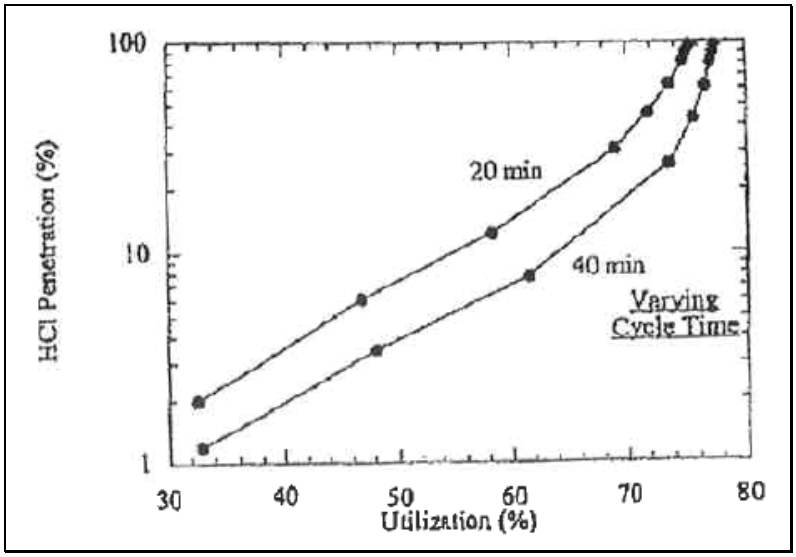

Figure 10: HCl penetration as a function of hydrated lime utilization at varying cycle times. Test was made with 19 % RH and 1000 ppm HCl at 120 °C.

4.2.2 Simultaneous absorption of HCl and SO_2

When HCl and SO_2 are studied simultaneously HCl and SO_2 penetration is a function of absorbent utilization. HCl penetration is predicted to be low while SO_2 penetration is high. For example to reduce HCl penetration to 10 %, hydrated lime utilization is approximately 40 %. At this utilization, 85 % of the SO_2 fed penetrates through the BHF. It is possible that absorbent recycle may make the use of hydrated lime more attractive for both HCl and SO_2 (Chrisholm and Rochelle, 1999) [4].

4.2.3 The effect of salts and RH to absorbent

The addition of salts such as calcium chloride to calcium-based absorbents has also been shown to improve acid gas absorption. Calcium chloride reduces the partial pressure of the water vapour over the solids

and as a result, a thicker layer of water adsorbs on the surface of the absorbent. If the RH is suiting it can lead to formation of bulk water on the surface of the absorbent. As the product layer comes thicker, the reactivity of HCl and SO_2 with the hydrated lime increases. The relation between increased RH and improved SO_2 absorption has been studied by Chrisholm in 1999 [4].

4.2.4 Other absorbent materials

Theoretic binding capacity of sodium is only half compared to calcium which means that amount of absorbent needed is double. Sodium bicarbonate is not as delicate to variations in combustion process as other absorbents and it has a large temperature range (90-300 ºC). Sodium bicarbonate is much more expensive than ordinary limes and it has to be grinded just before absorbing process so it becomes active.

4.3 The effect of HCl concentration to reduction

A study has been made with different HCl concentrations (Chrisholm and Rochelle 1999). The experiments resulted that with higher concentrations of HCl (~2000-3500 ppm); the increased HCl concentration decreased the HCl/Ca^{2+}-ratio (Figure 11).

One possibility to that is to be due to an increase in the plugging of the pores of the absorbent. Plugging happens in certain conditions and utilization becomes incomplete when pores become plugged near the external particle surface, leaving the interior of the absorbent unavailable for reaction.

When concentration is lower, surface of the solid allows for increased diffusion of the gas into the interior of the particle. Based on the study, HCl concentrations of 1000 ppm and lower are low enough to prevent plugging [4].

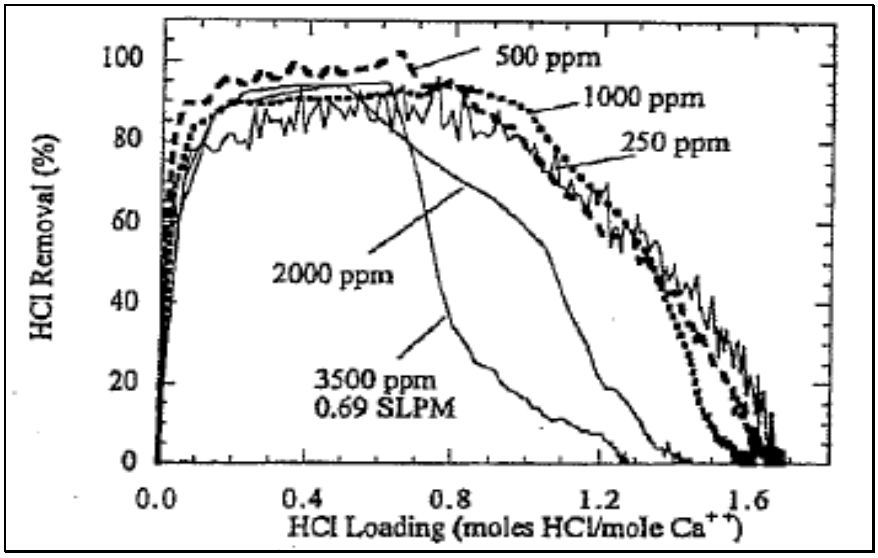

Figure 11: Effect of HCl concentration and HCl/Ca^{2+}-ratio on HCl removal. Experiments performed at 19 % RH and 120 °C.

4.4 The effect of the relation between HCl and SO_2

Studies of simultaneous absorption of HCl and SO_2 have been made with different absorbents. One study was with hydrated lime in a fixed-bed reactor at conditions simulating humidified flue gas dry scrubbing. Study was made by Chrisholm and Rochelle in 1999. The study was performed simulating the reaction conditions of acid gases with hydrated lime on a fabric filter for a municipal waste combustor. The reactor outlet concentration of the acid gases was measured continuously with an FTIR-spectrophotometer.

In the study it was discovered that when $CaSO_3$*½H_2O (Equation 5) is exposed to HCl vapour, SO_2 is evolved and $CaCl_2$*2H_2O is formed. Also, when $CaCl_2$*2H_2O is exposed to SO_2 in the absence of HCl, HCl is released by the solids and $CaSO_3$*½H_2O is formed. This is a reversible reaction [4].

$$CaSO_3 * ½H_2O + 2HCl + ½H_2O \leftrightarrow CaCl_2 * 2H_2O + SO_2 \qquad \textbf{(Equation 12)}$$

At early experimental times, the reactivity of SO_2 is limited by having to compete with HCl for alkalinity. Lower concentration of HCl increases SO_2 absorbance (Figure 12).

Later in the experiment, as the alkalinity of the absorbent became consumed, HCl reacts with $CaSO_3*½H_2O$, releasing SO_2 as indicated by equation 10. It was found that the concentration of SO_2 in the gas phase has little effect on the reactivity of HCl (
Figure 13).

When the ratio of SO_2/HCl in feed gas increases, slightly less $CaCl_2*2H_2O$ is formed in favour of a greater amount of $CaSO_3*½H_2O$. This suggests that there is pseudoequilibrium between the reaction products and the acid gases.

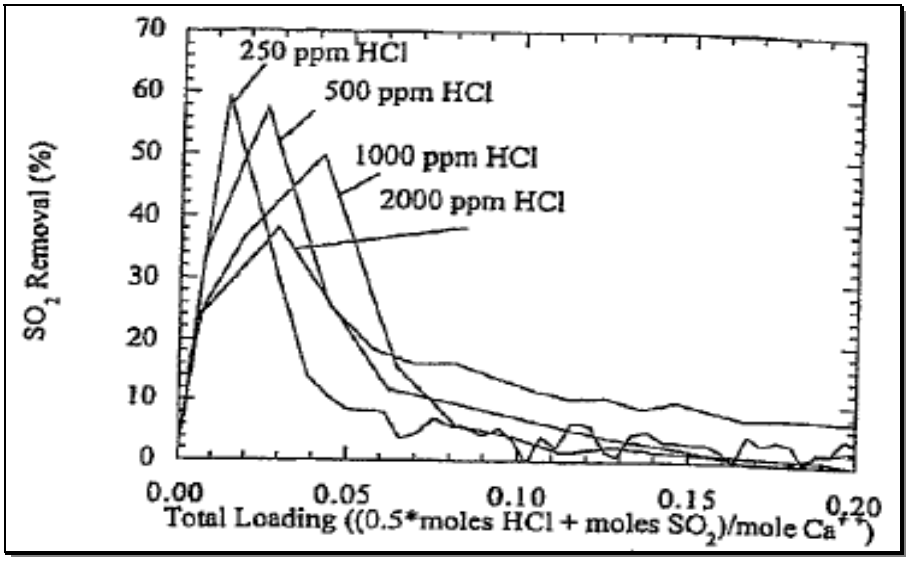

Figure 12: Effect of HCl concentration and total HCl+SO_2/Ca^{2+}-ratio on SO_2 removal. Experiments were made at 19% RH and 120 °C.

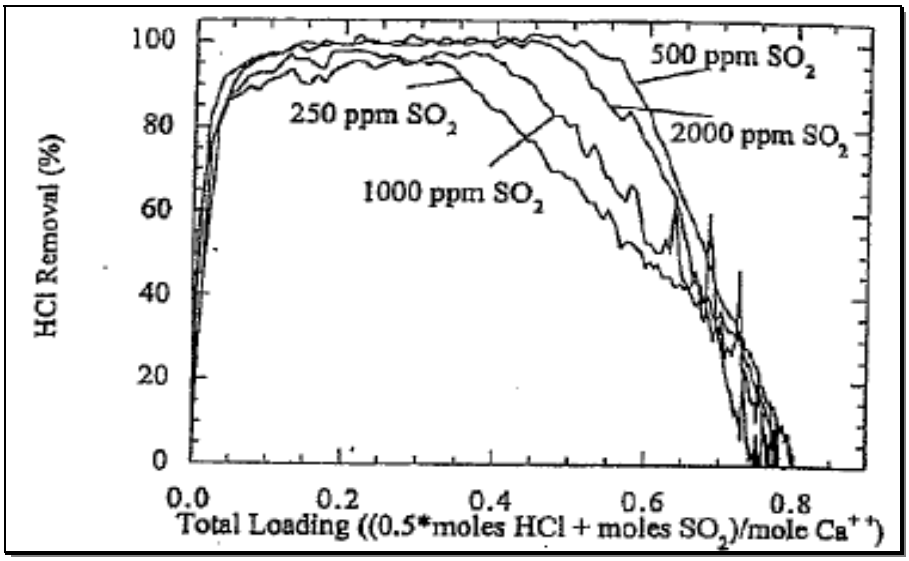

Figure 13: Effect of SO_2 concentration and total HCl+SO_2/Ca^{2+}-ratio on HCl removal. Experiments were made at 19 % RH and 120 °C.

4.5 The effect of O_2 on absorption process

The presence of O_2 in the feed gas leads to greater SO_2 removal and SO_2/Ca^{2+}-ratio according to a study by Chu and Rochelle in 1998 (used as reference in a study by Chrisholm and Rochelle 1999). It happens in the HCl-SO_2 gas mixture because S (IV) can be oxidized to S (VI) as in reaction (4). With a higher O_2 concentration, there is more S (VI) formed.

Early in the experiment there is a slight increase in SO_2 reactivity due to the presence of HCl with 5,5% O_2 also in the process. Once the alkalinity level gets lower, HCl reacts with $CaSO_3$*½H_2O causing SO_2 emissions. As the concentration of O_2 increases, the amount of sulphur that remained bound in the solids also increases.

For example with the amount of 250 ppm HCl and 1000 ppm of SO_2 in the gas stream, SO_2 does not have to aggressively compete with HCl. When the concentration of HCl is increased to 1000 ppm, the rapid absorption of HCl and consumption of alkalinity leads to reduced SO_2 reactivity (Figure 14).

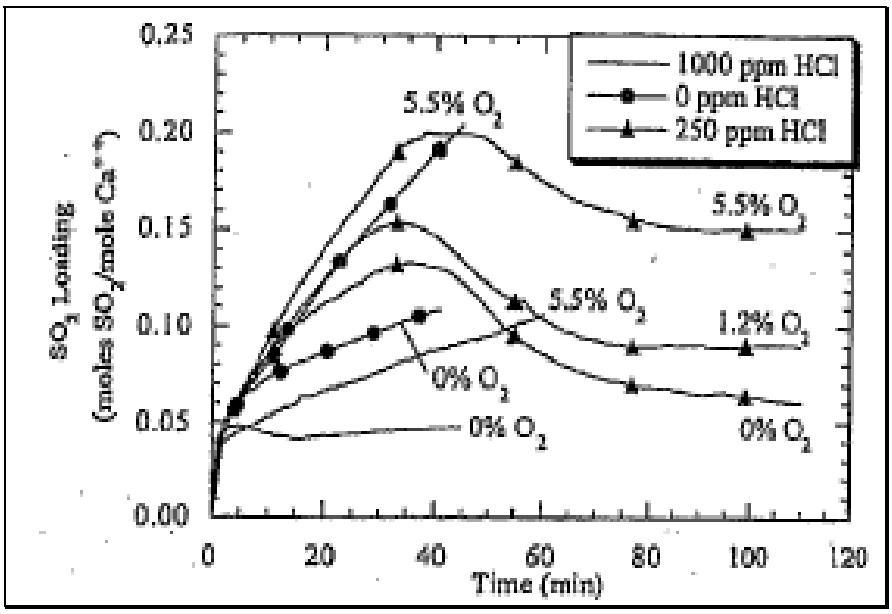

Figure 14: Effect of O_2 and HCl on loading of SO_2. Experiments were made at 19 % RH, 1000 ppm SO_2 and 120 °C.

In summary, if SO_2 does not have to compete with HCl for alkalinity, it reacts almost as if the HCl is not in the feed gas. Once SO_2 reacts, the presence of O_2 in the gas stream allows the irreversible oxidation of S (IV). But the oxidation does not take place quickly enough to force all the bound sulphur to S (VI).

Consequently, SO_2 is emitted as HCl begins to break through to the end of the reactor. At a high HCl concentration, SO_2 has to compete with HCl for alkalinity. This competition causes a reduction in SO_2 activity, even in the presence of O_2 [4].

4.6 The effect of NO_x on the absorption process

In general about 90 % of NO_x is NO_2 and the remaining 10 % is NO. In a study by Nelli and Rochelle in 1998, (used as reference in a study by Chrisholm and Rochelle 1999) was found that increasing NO_2 concentration improves SO_2 reactivity. The study was made without HCl in the process. NO_2 acts as an catalyst promoting S (IV) oxidation or participate directly in S (IV) oxidation [4].

$$Ca(OH)_2 + CaSO_3 * ½H_2O + 2NO_2 + ½H_2O \rightarrow CaSO_4 * 2H_2O + Ca(NO_2)_2$$ **(Equation 13)**

With O_2 in the feed, final SO_2/Ca^{2+}-ratio rises even more. Even as the solids are approaching complete utilization, the absorption of SO_2 continues. The improved SO_2 absorption is probably due to enhanced absorbent utilization from the formation of sulphur-nitrogen compounds. Greater SO_2 concentration also enhances NO_2 absorption. Addition of NO to SO_2 does not chance SO_2/Ca^{2+}-ratio at any way. Absorption of SO_2 and NO_2 can be observed without those gases having to compete with HCl for alkalinity by keeping HCl levels low enough (~250 ppm).

The addition of 250 ppm HCl to the system increases the NO_2/Ca^{2+}-ratio. However, adding the O_2 causes a reduction in the ratio of NO_2. It is because O_2 in the feed stream oxidizes S (IV) and it cannot react with NO_2 by reaction (11). The reaction with HCl does not chance considerably with the addition of NO_2. Even when HCl has to compete the most for alkalinity, its reactivity still suffers only minimally as is seen in the Table 4.

Table 4: Final ratios of HCl, SO_2 and NO_2. Amounts of substances are 250 ppm HCl, 1000 ppm SO_2, 2,5 % O_2 and 150 ppm NO_2.

	HCl (mol of HCl/mol of Ca^{2+})	SO_2 (mol of SO_2/mol of Ca^{2+})	NO_2 (mol of NO_2/mol of Ca^{2+})
HCl and SO_2	1,58	0,06	-
+ NO_2	1,34	0,31	0,10

4.7 The effect of process conditions to furnace injection

Study by (Partanen et al.) about simultaneous absorption of HCl and SO_2 showed a cross-sectional SEM (scanning electron microscopy) image of a particle that has simultaneously reacted with HCl and SO_2 at 850 °C for 10 minutes. Interestingly, sulphur can be found also in the inner parts of the particle. Chlorine appears to be rather evenly distributed inside the particle as well (Figure 15) [3].

A possible explanation for the differences in the formation of the product phase as well as for the enhanced sulphation during the simultaneous absorption of HCl and SO_2 is the formation of a molten product phase in the absorbent particles according to the study. That is also reported in the study by Matsukata et al. (1996) [6]. Results by Partanen et al. imply that the explanation for the improved sulphation is the formation of molten phases at 650°C.

It was observed that large agglomerates were formed in absorbent particles that had reacted at 650 °C. The formation of such agglomerates implies that melting of the particles most likely occurs in the sample at 650 °C as well when sulphation and chlorination occur concurrently.

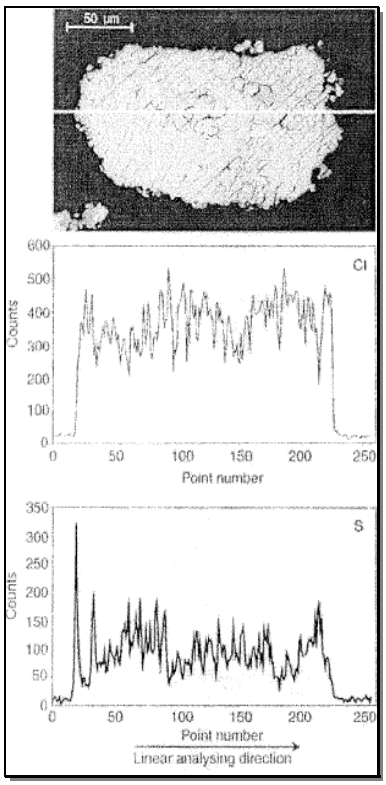

Figure 15: Distribution of chlorine and sulphur inside a calcined limestone particle after a reaction with a gas stream of HCl, SO_2, O_2 and N_2 at 850 °C; reaction time 10 minutes.

4.7.1 The effect of HCl to SO_2 absorption in the furnace

In combustion systems, the presence of limestone is usually to capture SO_2 emissions. The effect that HCl has on the sulphation of CaO is researched by i.e. Lawrence and Bu in 2000. Experiments were made in three temperatures; 680, 750 and 850 °C (Figure 16**,** Figure 17).

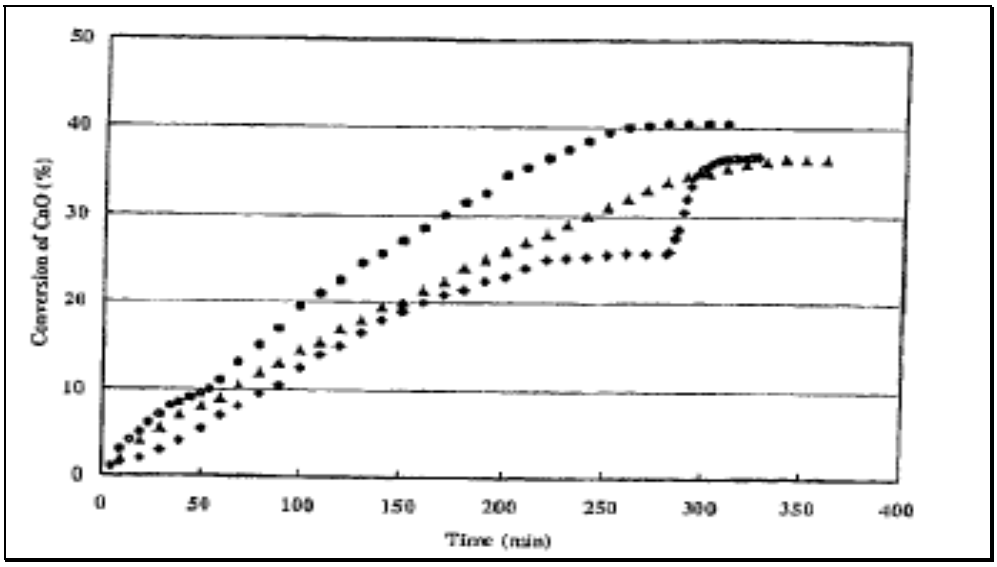

Figure 16: The sulphation of CaO at 680 °C (♦), 750 °C (▲) or 850 °C (●) in the presence of 2300 ppm SO_2 and 5 % O_2.

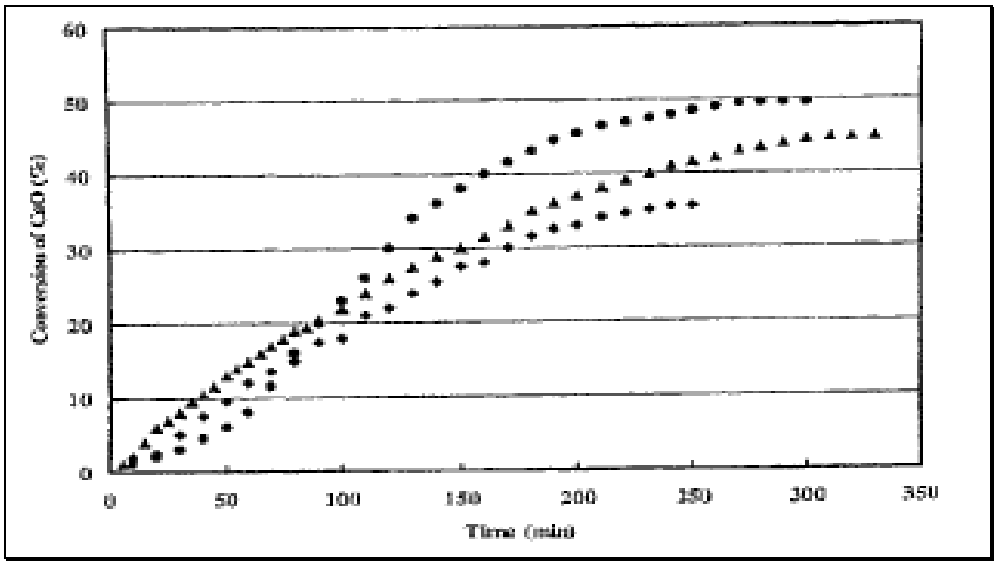

Figure 17: The sulphation of CaO at 680 °C (♦), 750 °C (▲) or 850 °C (●) in the presence of 2300 ppm SO_2, 2000 ppm HCl and 5 % O_2.

There are two changes when temperature is increased. First, there is a slight increase in the rate of sulphation of the limestone and secondly, the final conversion of CaO increases with increasing temperature. Because the molar volume of $CaSO_4$ is greater than that of CaO, as calcium oxide is sulphated, the forming sulphate layer on the outside of the particle and in the pores, blocks access to unreacted CaO in the centre of the particle.

Addition of HCl increases the conversion of CaO by 12-37 %. When HCl is added to the fluidized bed there is a further reaction between the SO_2 and unreacted CaO. The presence of HCl increases the conversion of CaO at all temperatures by around 20 % [7].

4.7.2 The effect of temperature variation

The effect of temperature variation on reducing emissions has been studied i.e. the study by Matsukata et al. in 1996. Study investigated chlorination and sulphation of calcined limestone at ~630-930 °C (900-1200 K). Study clearly indicates that the temperature of a fluidized bed significantly affects the efficiency of dechlorination in the presence of 10 % steam (Figure 18). Efficiency of dechlorination in FBC's heavily depends on the concentration of steam in the temperature range commonly used in FBC's (630-930 °C). The efficiency of HCl retention, i.e. the percentage of dechlorination, decreases with increasing concentration of H_2O (Figure 19).

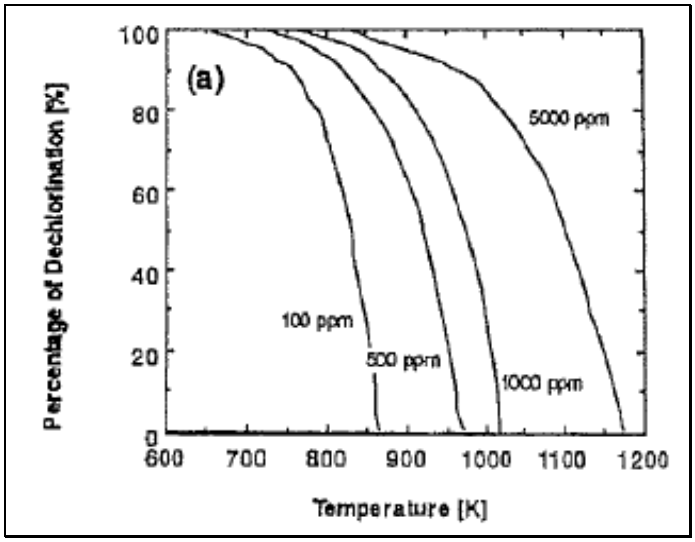

Figure 18: Temperature dependency of the percentage of dechlorination for different HCl concentrations in the presence of 10 % H_2O.

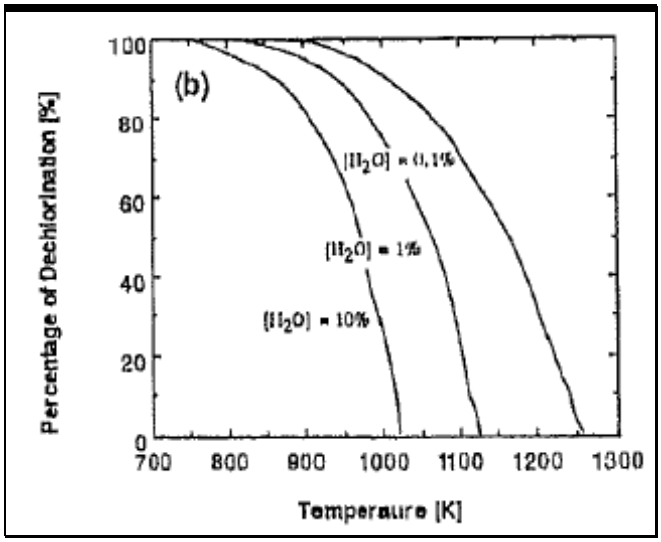

Figure 19: Temperature dependency of the percentage of dechlorination for different H_2O concentrations.

At higher concentrations of H_2O and higher temperatures, the HCl emission control is thermodynamically restricted [6].

According to research (Matsukata et al. 1996) [6] the chlorination of calcined limestone can result in the formation of aggregates and voids in or on the calcined limestone particles. These voids are able to allow SO_2 to readily enter into the bulk of CaO particles. Moreover, the product of chlorination, $CaCl_2$, probably reacts with $CaSO_4$ forming a eutectic phase to lower the melting point. It was considered that such a molten phase can cause the recovery of SO_2 absorption capacity with calcined limestone.

Another experiment studying simultaneous absorption of HCl and SO_2 is made by Partanen et al. in 2005. Tests were made at 850 °C, one for independent chlorination and the other for the simultaneous absorption. As shown in the Figure 20, CaO is effectively converted to $CaCl_2$ in the absence of SO_2 at 850 °C. However, when simultaneous sulphation occurred, very low concentrations of $CaCl_2$ are achieved. Furthermore, the slope of the chlorination curve turns negative as the reactions within the sample proceeds, leading to values close to zero by the end of the reaction time.

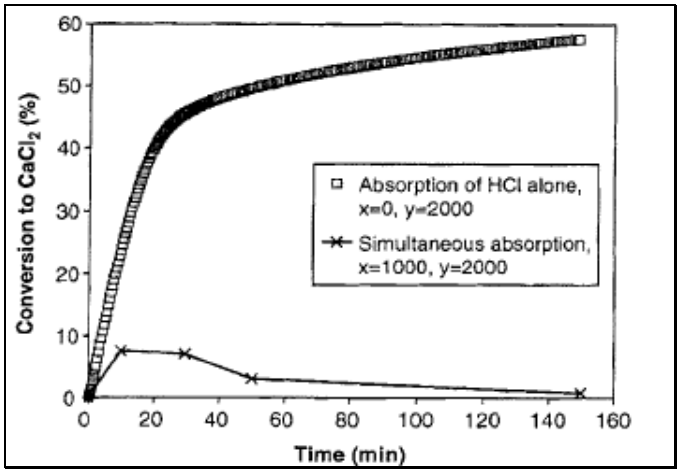

Figure 20: Conversion of CaO to $CaCl_2$ versus time at 850 °C; simultaneous absorption with SO_2 versus independent absorption. Sample was diluted with Al_2O_3. Gas composition: x ppm SO_2, y ppm HCl and 5% O_2 in N_2.

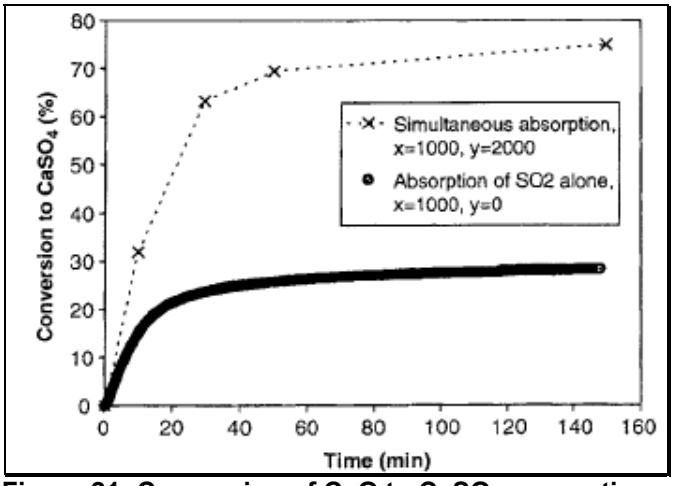

Figure 21: Conversion of CaO to $CaSO_4$ versus time at 850 °C; simultaneous absorption with HCl versus independent absorption. Sample was diluted with Al_2O_3. Gas composition: x ppm SO_2, y ppm HCl and 5% O_2 in N_2.

On the other hand, a considerable enhancement is seen in the sulphation of CaO due to the simultaneous chlorination of the absorbent. This result is illustrated in Figure 21. When independent sulphation occurs at 850 °C, a conversion to $CaSO_4$ of only approximately 27 % is reached. However, when HCl is also present in the reacting gas, a conversion of close to 75 % is achieved for sulphation in 10 minutes of reaction time.

In figures, (Figure 22, Figure 23) results are shown for otherwise similar experiments although this time the reaction temperature is 650 °C. The results shown in the figures clearly indicate that the simultaneous sulphation suppresses the attainable conversion to calcium chlorides at 650 °C as well. They other hand confirm that much higher conversions to $CaSO_4$ are attainable at 650 °C as well when the simultaneous chlorination of CaO occurs.

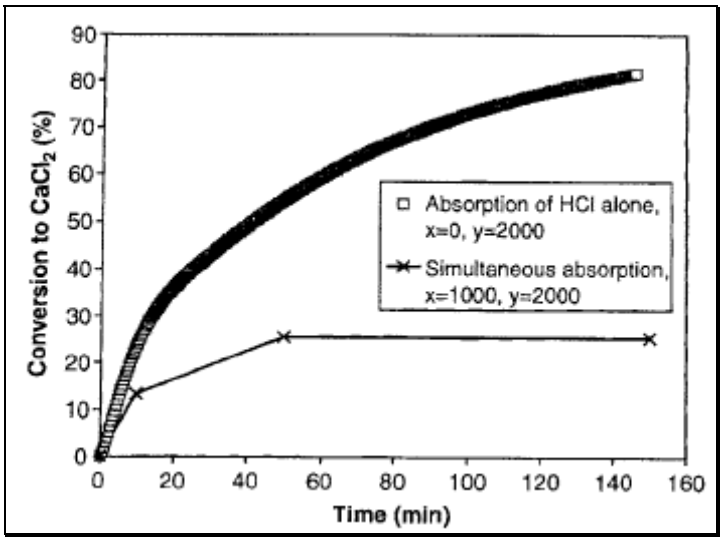

Figure 22: Conversion of CaO to $CaCl_2$ versus time at 650 °C; simultaneous absorption with SO_2 versus independent absorption. Sample was diluted with Al_2O_3. Gas composition: x ppm SO_2, y ppm HCl and 5% O_2 in N_2.

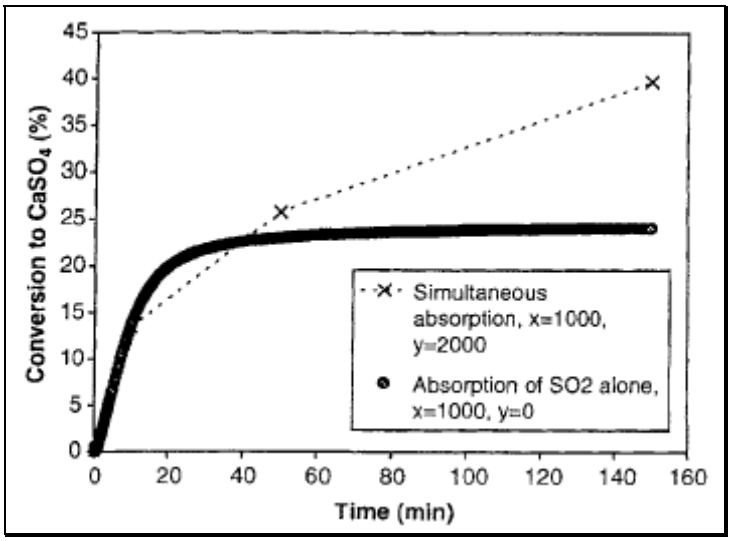

Figure 23: Conversion of CaO to $CaSO_4$ versus time at 650 °C; simultaneous absorption with HCl versus independent absorption. Sample was diluted with Al_2O_3. Gas composition: x ppm SO_2, y ppm HCl and 5% O_2 in N_2.

One possible explanation for the suppressed and decreasing levels of chlorination could be that some reaction that consumes the product of chlorination occurs; for example, subsequent reactions from $CaCl_2$ to $CaSO_4$ could explain the results. As well, such reactions would offer an alternative explanation for the improved sulphation observed when chlorination occurs at the same time. It is proposed that the following overall reactions may play a potential role in the process of concurrent sulphation and chlorination [3].

$$CaCl_2(s,l) + SO_2(g) + O_2(g) \Leftrightarrow CaSO_4(s) + Cl_2(g) \quad \textbf{(Equation 14)}$$

$$2CaCl_2(s,l) + 2SO_2(g) + O_2(g) + 2H_2O(g) \Leftrightarrow 2CaSO_4(s) + 4HCl(g) \quad \textbf{(Equation 15)}$$

To conclude, there appear to be two possible mechanisms that could explain the phenomenon of enhanced sulphation. One relates to the formation of molten phases in the absorbent particles. A molten product phase is accompanied by a much smaller diffusional limitation for further reaction than is a solid product layer. Melting could also lead to morphological changes on the absorbent surface and create diffusion paths that enable further reaction.

Experiments indicate that HCl is able to penetrate through the sulphate layer and react with the calcium beneath the layer. Thereafter, the product layer obviously melts, even at rather low temperatures, opening

the particle for further sulphation. This mechanism of molten phase formation cannot, however, explain the suppressed chlorination of CaO and $CaCO_3$ observed during the simultaneous absorption of SO_2 and HCl.

A likely explanation of both the enhanced sulphation and suppressed chlorination is that the calcium chloride initially formed is consumed in a subsequent reaction with SO_2. Such a reaction would improve the yield of the sulphate product and lower the level of absorbent chlorination.

The enhancement of SO_2 absorption should lead to a more efficient utilization of the absorbent and lower the costs of SO_2 control. One drawback in this, however, is the potential partial melting of the absorbent particles during the combustion process, which might promote fouling of the boiler or lead to agglomeration problems in the bed. Moreover, according to Partanen, it does not appear to be possible to capture HCl and SO_2 simultaneously by limestone at the temperatures prevailing in fluidized bed combustors [3].

4.7.3 The effect of absorbent

In a study by Matsukata et al. in 1996, chlorination is studied in the presence and absence of SO_2. Figure 24 compares the progress of chlorination with different particle sizes. According to the study, 2Cl/Ca ratio slightly depends on limestone's particle size in the initial stage but those with different sizes almost overlaps after 90 minutes on stream. That finding is different than findings in the study by Daoudi and Walters 1991 (used as reference in a study by Matsukata et al.). Study reports that chlorination rate decreases with increasing particle size.

Sulphation of limestone happens in following way. Numerous pores are generated during the calcination of limestone. These pores serve as paths for the diffusion of SO_2 into the interior of a limestone particle. Pore closure occurs with the progress of sulphation with SO_2 resulting in the deterioration of the activity for sulphation and sulphation finally stops after the pores are fully closed. As a result, the outer surface area of calcined limestone is a dominant factor governing the sulphation rate. That is, the rate of sulphation of calcined limestone heavily depends on its particle size.

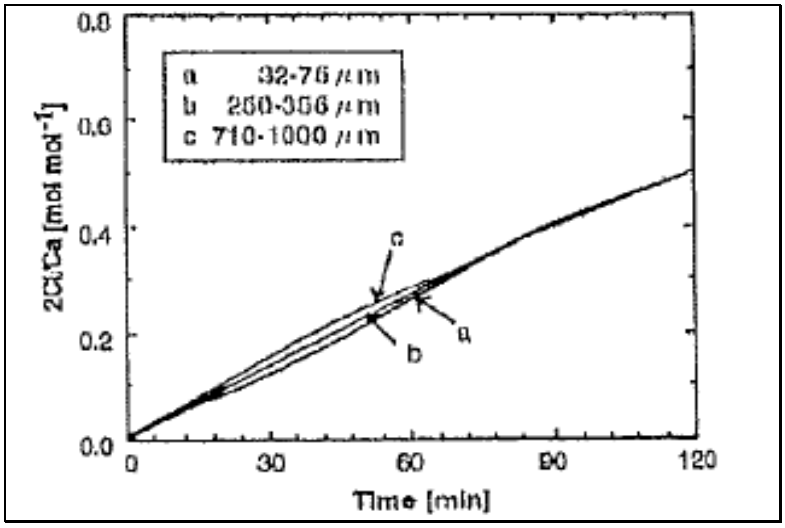

Figure 24: Progress of chlorination of calcined limestone at 1023 K. Particle size of limestone used is in the three ranges of 32-75, 250-355 and 710-1000 μm.

As to HCl absorption, the simultaneous presence of SO_2 hardly influences the chlorination behaviour, while the chlorination rate of calcined limestone seems to be slightly depressed in the presence of SO_2 (Figure 25). On the other hand, significant effect of coexisting HCl is observed on the sulphation of calcined limestone as seen in Figure 26. Sulphation is markedly accelerated in the presence of HCl. The acceleration of sulphation becomes remarkable for larger limestone. The results using the smallest particle size is an exception.

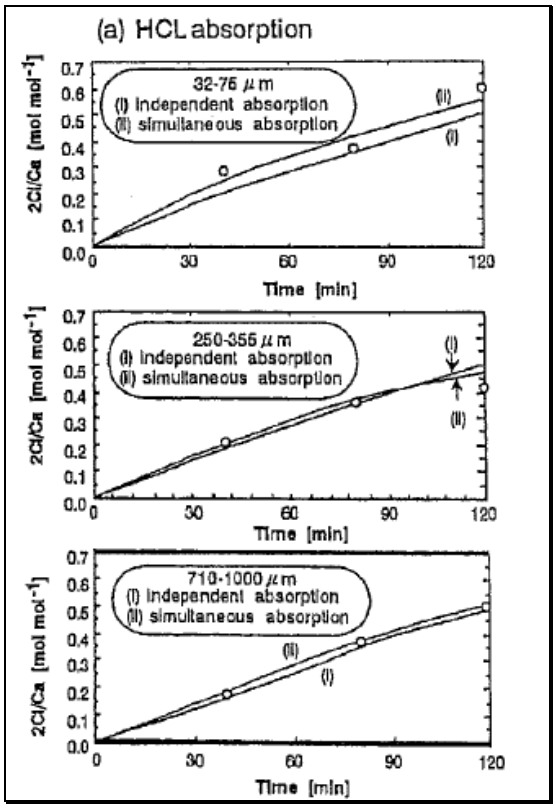

Figure 25: Progress of chlorination of calcined limestone in the presence and absence of SO_2. Both concentrations of HCl and SO_2 were 1000 ppm.

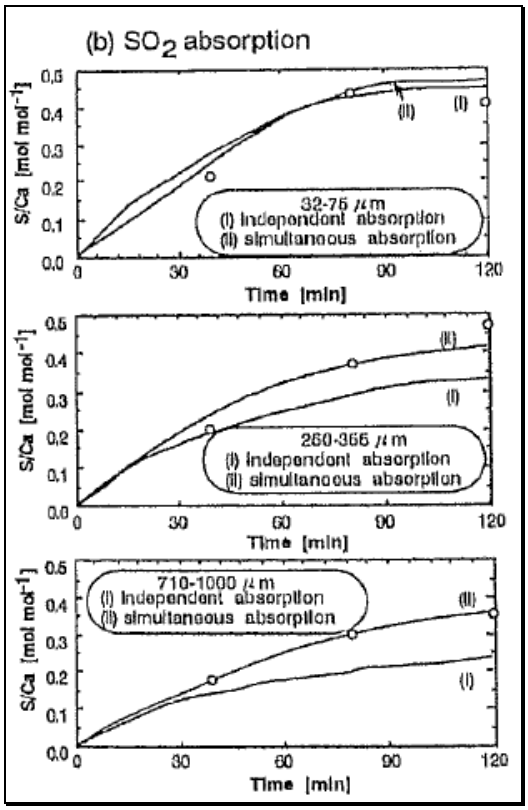

Figure 26: Progress of sulphation of calcined limestone in the presence and absence of HCl. Calcined limestone with three different ranges of particle size were used. Both concentrations of HCl and SO_2 were 1000 ppm.

The absorption capacity of limestone for SO_2 is enhanced even at temperatures lower than the melting point of $CaCl_2$. Since the deterioration of absorption activity for SO_2 with time on stream is mainly due to pore closure, this tendency implies that the presence of HCl has a role in it. Large voids that are generated in chlorination seemingly play as a role of paths through which the interior of a limestone particle is easily accessible to HCl. Namely, while the formation of $CaSO_4$ leads to pore closure in the absorption of SO_2, the paths for HCl diffusion from the outer surface to the interior of a limestone particle are created in the course of the HCl absorption by the formation of the aggregates and the resultant voids.

When HCl and SO_2 are simultaneously absorbed, a molten phase composed of eutectic mixture of $CaCl_2$ and $CaSO_4$. Mixture melts at 724 °C which is much lower than the melting point 772 °C. The voids among aggregates possibly play a role of paths for the diffusion of HCl and SO_2 toward the interior of limestone particles. However, the melting of the eutectic mixture possibly contributes to the promotion of SO_2 absorption more largely at higher temperatures as high as 950 °C used in the study (Matsukata et al.) [6].

4.8 Conclusions

The parameters that affect the absorption of HCl and SO_2 are relative humidity, concentration of the gas, relation between HCl and SO_2, presence of oxygen, presence of NO_x as well as the amount and quality of the absorbent and temperature of the gas (temperature studies only made with furnace injection) (Figure 27, Figure 28).

Relative humidity is very important process element in the reduction of HCl as well as to SO_2. Increasing relative humidity increases the reduction of HCl and SO_2. In independent absorption of HCl, higher concentration of HCl causes lower utilization of absorbent. It is because of plugging of the pores of the absorbent. In simultaneous absorption, reactivity of SO_2 is limited, because of competition with HCl for alkalinity. Lower concentrations of HCl improve SO_2 absorption. Concentration of SO_2 does not affect HCl reactivity.

There is a relation between HCl and SO_2 amounts. As the ratio of SO_2/HCl increases, HCl reduction is reduced in favour of a greater reduction of SO_2 (pseudoequilibrium).

Presence of oxygen improves the reduction of SO_2 because of oxidation of S (IV) to S (VI). Higher concentrations of HCl cause a reduction in SO_2 activity, even in the presence of oxygen. Oxygen doesn't affect HCl reactivity.

Increasing concentrations of NO_2 improve SO_2 reactivity. Presence of oxygen improves the reactivity even further enhancing the absorbent utilization. Greater SO_2 and HCl concentrations also increase NO_2 absorption. NO does not effect in SO_2 in any way. Reduction of HCl is slightly reduced in the presence of NO_2.

The parameters that improve absorbents efficiency are BET area, fly ash, particle size, cleaning cycle and absorbent feed ratio. Bigger BET area and a certain amount of fly ash improve cleaning capacity in the bag house filter. Smaller particle size improves mixing of absorbent and flue gas and improves efficiency. Longer cleaning cycle should improve absorption at least in theory. Absorbent feed ratio effects in absorbent utilization. When feed ratio increases, utilization decreases. Lower absorbent utilization improves HCl reactivity. In simultaneous absorption HCl reduction is high when SO_2 reduction is low. The conditions that maximise absorbent utilization are high relative humidity, SO_2, NO_2 and O_2 concentration and low HCl concentration.

The addition of salts to absorbents improves HCl and SO_2 absorption. Salt addition results into a thicker layer of water on the surface of absorbent and improve gas reduction.

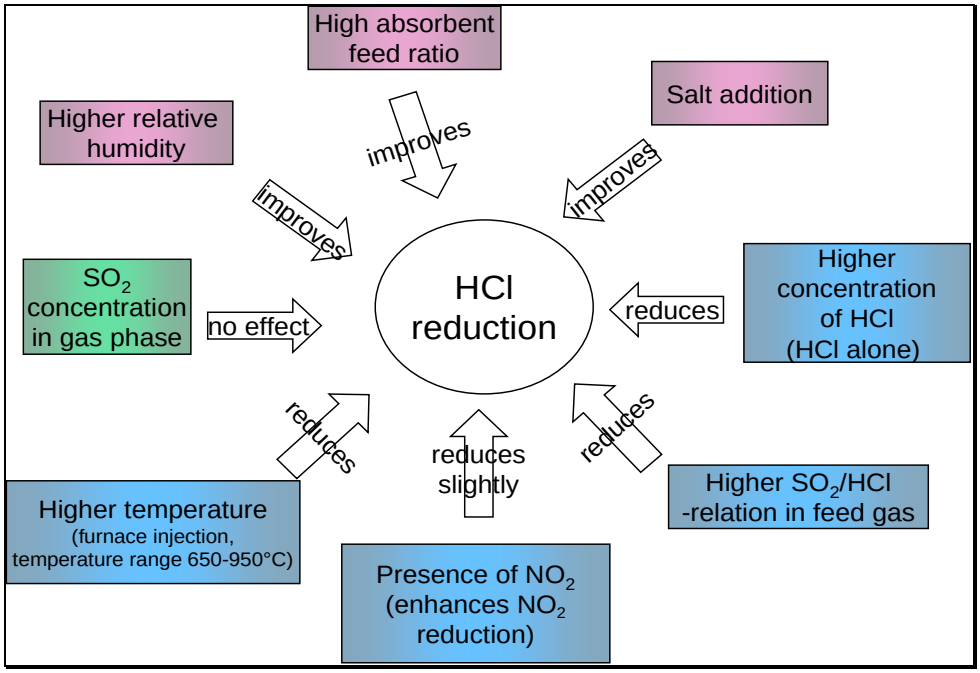

Figure 27: Parameters that affect HCl reduction.

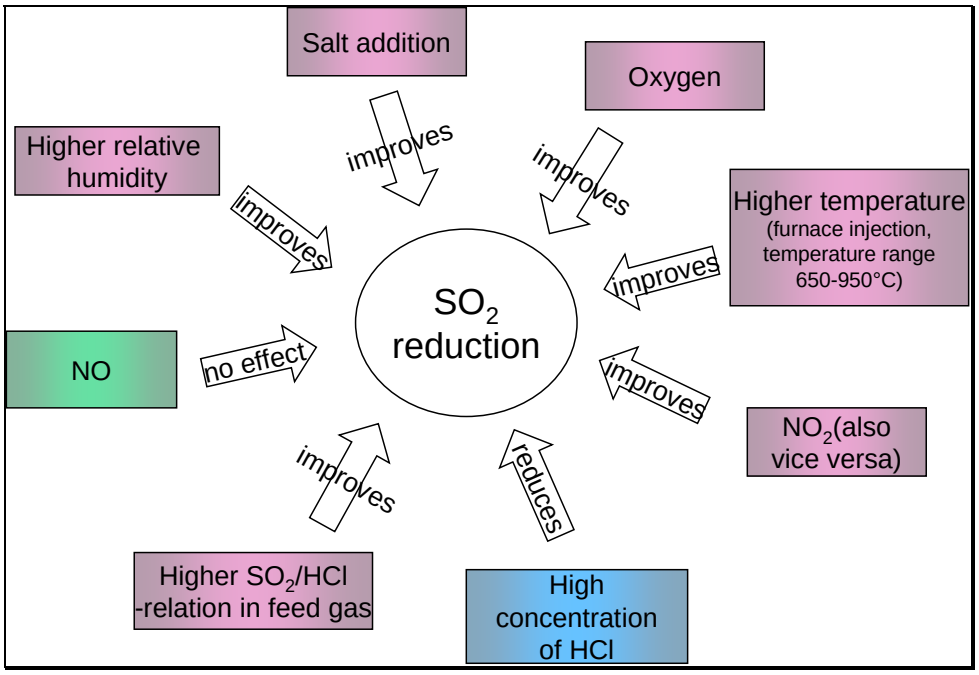

Figure 28: Parameters that affect SO_2 reduction.

5. MEASUREMENT EXECUTION

5.1 Test site

The experiments were carried out at a bubbling fluidized bed (BFB) boiler in Finland. The boiler is shown in Figure 29. Fuels used in this BFB boiler are bark, forest residue, peat, sludge and recycled fuel. Mixing between air and fuel is good and its combusting temperatures can be controlled. Boiler start-up was in 2006 [11].

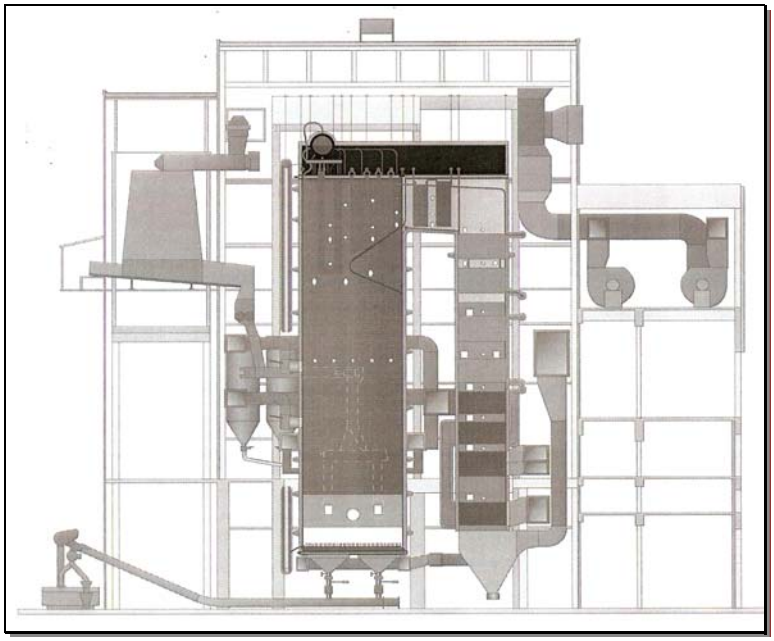

Figure 29: BFB Power boiler where the tests were made.

5.2 Experimental set-up

During the test run boiler load was set and kept as constant as possible during the experiments. Experiments were made with larger and smaller load. The main test conditions are shown in Table 5.

The purpose of the dryer was to adjust the moisture of the fuel fed into the furnace. Fuel's dry solids content was 60% after the dryer. Drying the fuel increases its heat value.

Table 5: Test points that were carried through

Day	Test number	Time	Temperature before filter (°C)	Fuel dryer (on/off)	Lime feed (on/off)	Load (kg/s) solid
Monday	1	14:30-17	156	on	on	30
	2	19-24	143	on	on	30
		03		off		
Tuesday	3	9:30-13:45	156	off	on	30
	4	15-16:30	156	off	on	30
	5	20-24	143	off	on	30
		22		on		
		03			off	
		05		off		
		06		off	off	30->20
Wednesday	6	8-12	140	off	off	20
	7	14-17	160	off	off	20
	8	22-02	160	on	off	20
Thursday	9	8-11:30	140	on	off	30
	10	13-15	160	on	off	30

5.2.1 Limestone

Limestone feed into the furnace was carried out from a limestone silo. When the feed was on, its rate was kept constant at 50 kg/h.

5.2.2 Fuel

Fuel used in the boiler was a mixture of wood waste, sludge and REF. Fuel composition was not constant during tests (Figure 30, Figure 31).

Figure 30: Fuel mixture.

Figure 31: Fuel mixture.

5.3 Flue gas analysers

Emissions (especially HCl and SO_2) were analysed by a Gasmet FTIR spectrometer (Fourier Transform Infra Red Spectrometer). It was installed in the flue gas duct before bag house filter in ~1m depth (Figure 1).

Plant stack emissions were also followed. They were performed with Gasmet FTIR spectrometer.

There were some errors in the measurements because of adjusting of the measuring equipment. These values were left out of the data.

5.4 Monitored emissions

Monitored gas components during the test run were:
H_2O, CO_2, CO, NO_x, SO_2, NH_3, HCl and O_2.

Main interest was in the acid gases (HCl and SO_2). Variations of these gases and minimum and maximum values during tests are in the figures below (Figure 32-Figure 35).

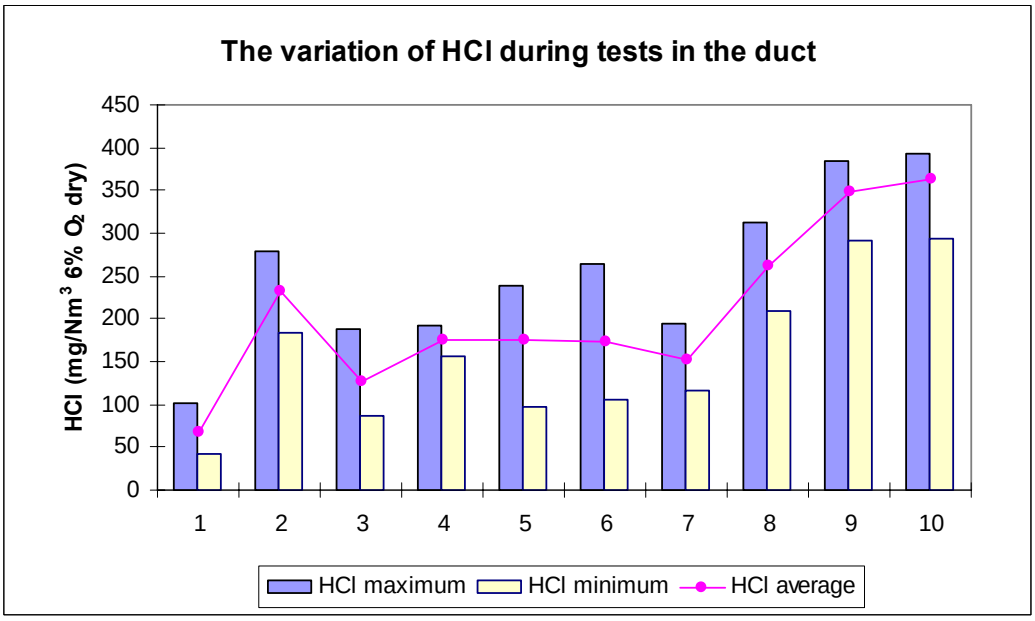

Figure 32: The variation of HCl during the tests measured in the flue gas duct. Measurements of HCl were mg/Nm^3 6 % O_2 dry. These are average values during the whole test period (tests 1-10).

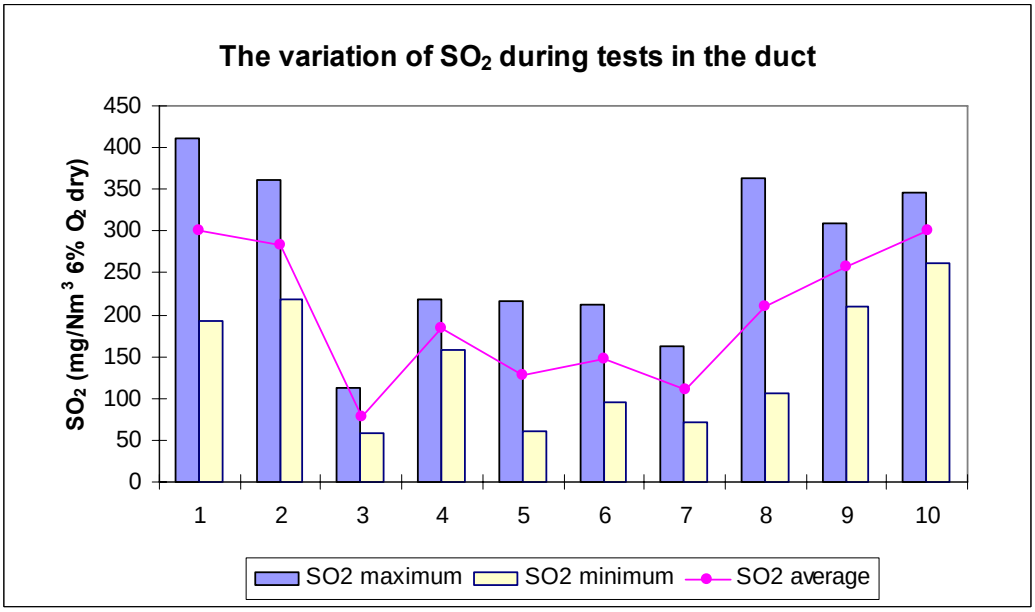

Figure 33: The variation of SO_2 during the tests measured in the flue gas duct. Measurements of SO_2 were mg/Nm^3 6 % O_2 dry. These are average values during the whole test period (tests 1-10).

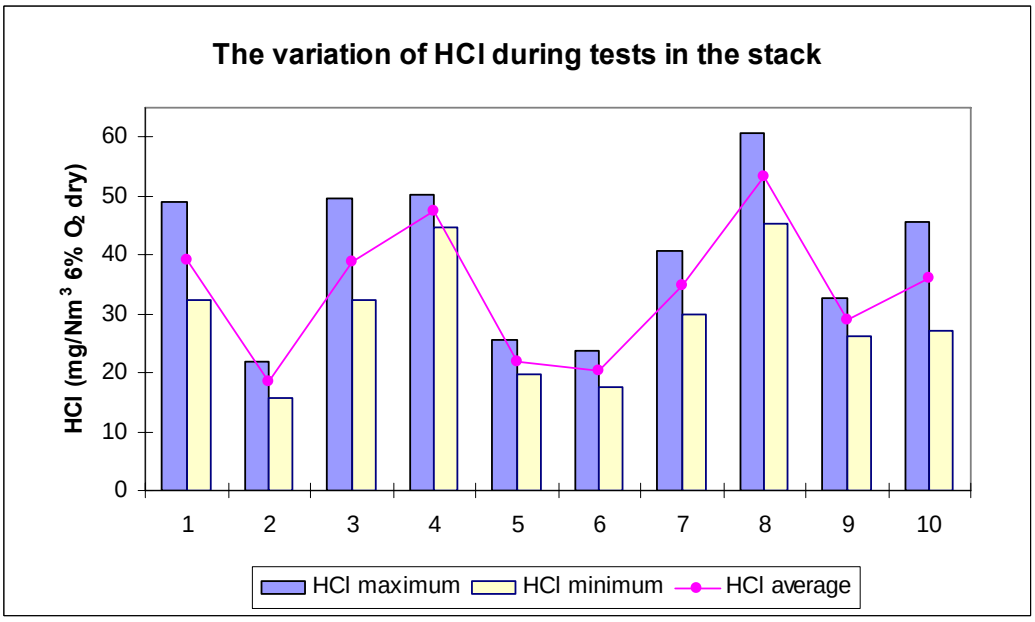

Figure 34: The variation of HCl during the tests measured in the stack. Measurements of HCl were mg/Nm^3 6 % O_2 dry. These are average values during the whole test period (tests 1-10).

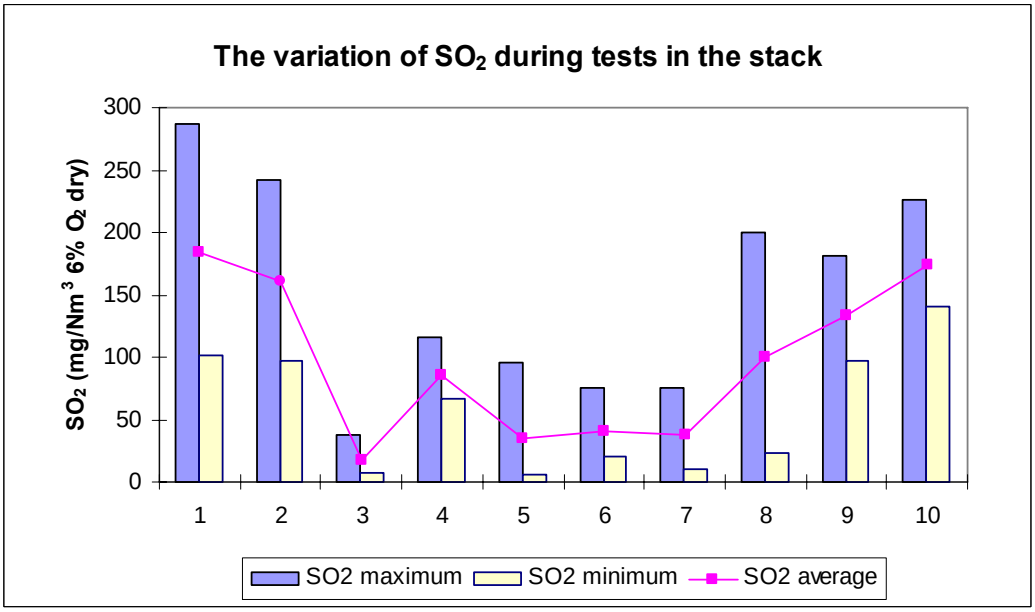

Figure 35: The variation of SO_2 during the tests measured in the stack. Measurements of SO_2 were mg/Nm^3 6% O_2 dry. These are average values during the whole test period (tests 1-10).

6. MEASUREMENT RESULTS

6.1 The effect of flue gas moisture content

Figure 36 shows the relation between flue gas absolute and relative moisture in different temperatures. Measurements were made from the flue gas duct. Relative humidity is calculated according to equations 10 and 11. As can be seen in the figure, relative humidity is higher when absolute moisture is higher and temperature is lower.

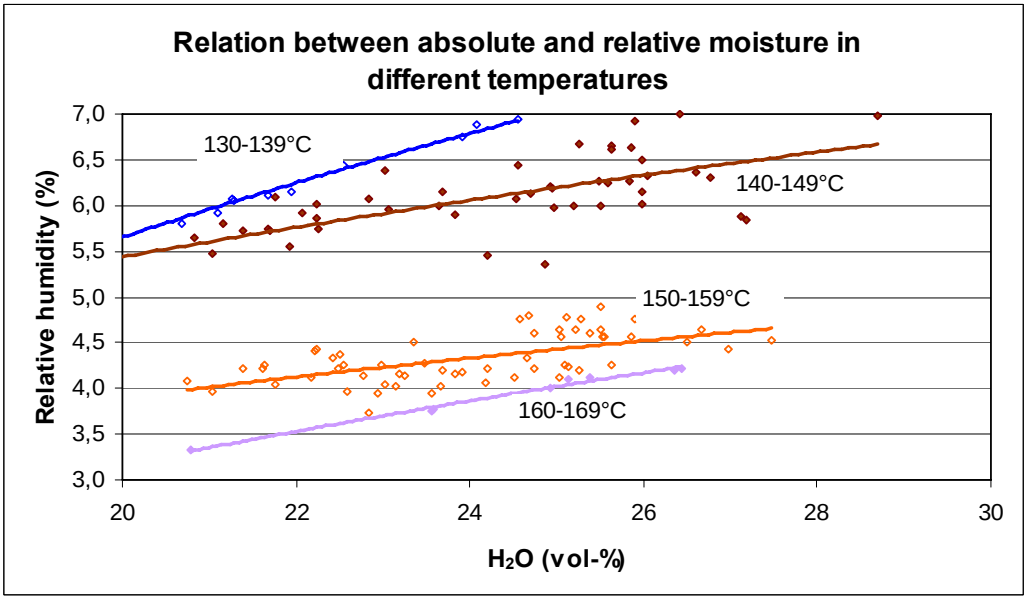

Figure 36: The relation between flue gas absolute and relative moisture in different temperatures. Values are averages (15 minute periods) during the whole test period (tests 1-10).

Figure 37 shows how fuel dryer affected fuel moisture and flue gas absolute moisture. According to the figure drying lowered fuel moisture ~ 10-% units and absolute moisture ~ 5 %-units.

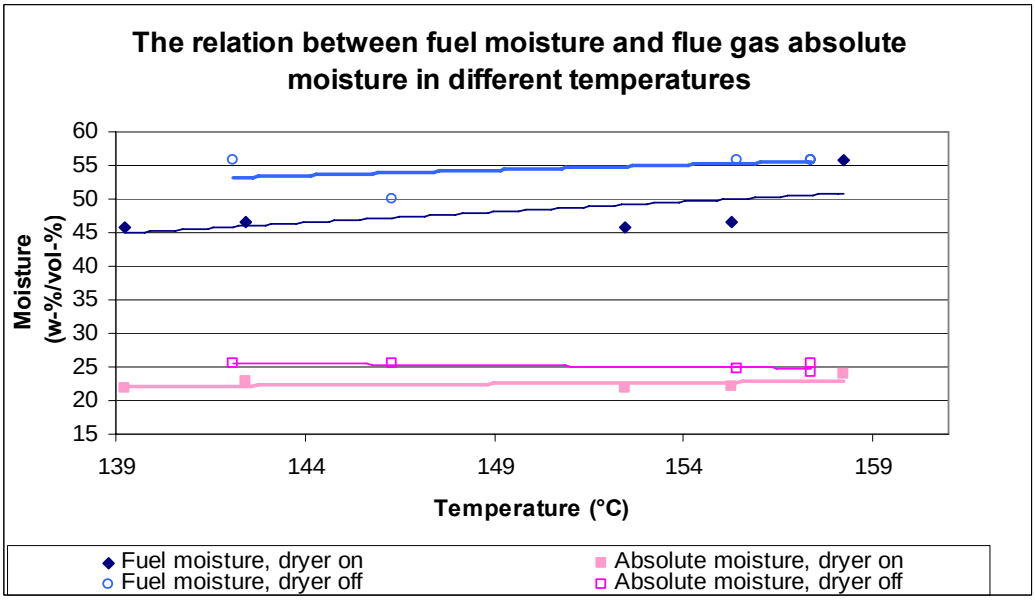

Figure 37: The relation between fuel moisture and flue gas absolute moisture in different temperatures. These are average values from each test point.

6.1.1 The effect of relative humidity

Figure 38 and Figure 39 show the variation of HCl and SO_2 during the test period as a function of relative humidity. Values are measured from the flue gas duct and from the stack. There are scattering in the other values, but contents in the stack for HCl seem to be decreasing with increasing relative humidity. Variation of gases is because of changes in the fuel mix.

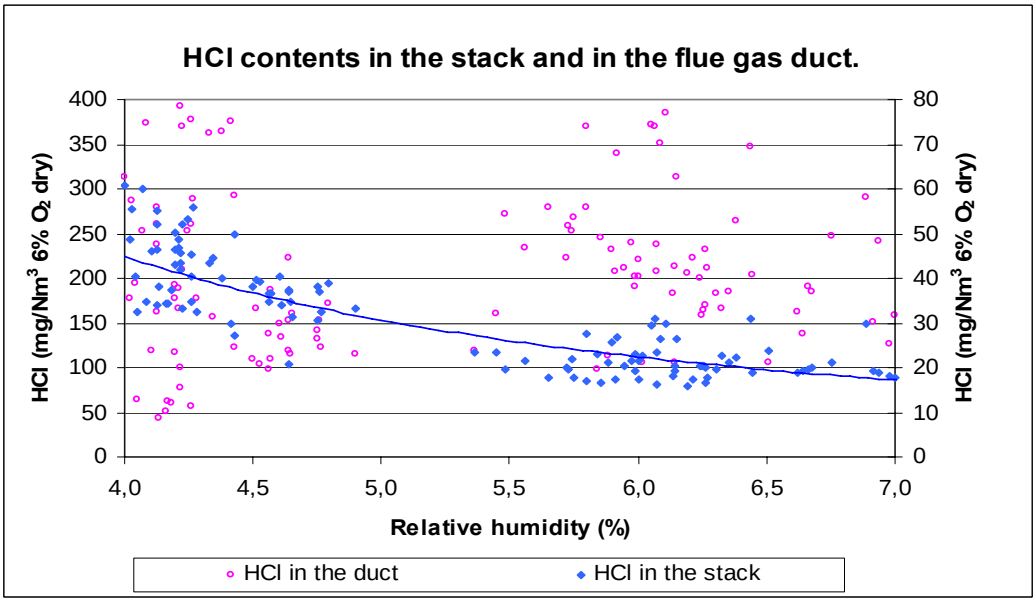

Figure 38: The variation of HCl in the stack and in the flue gas duct during tests as a function of relative humidity. Values are averages (15 minute periods) during the whole test period.

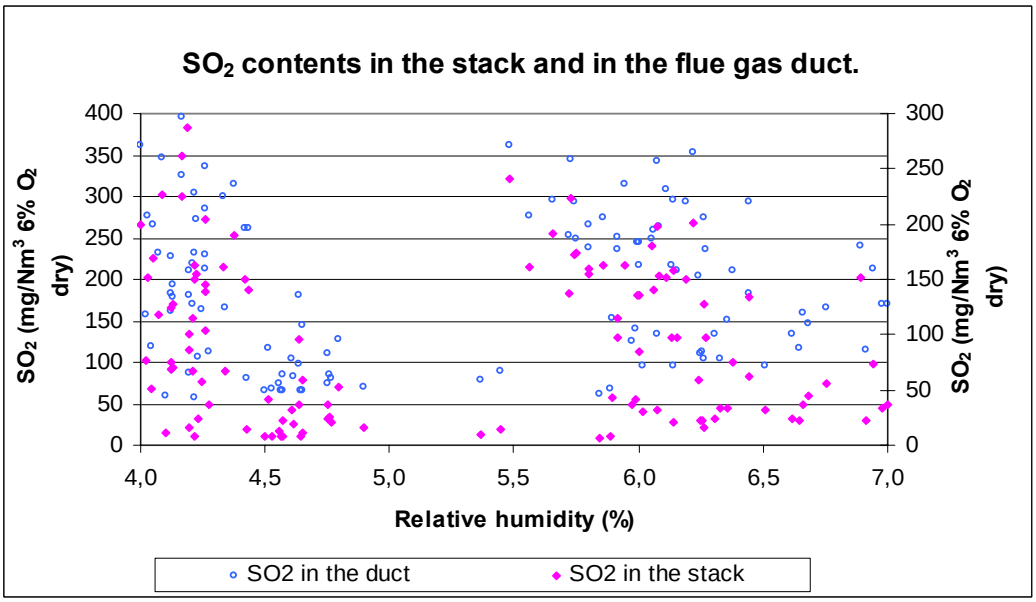

Figure 39: The variation of SO_2 in the stack and in the flue gas duct during tests as a function of relative humidity. Values are averages (15 minute periods) during the whole test period.

Figure 40 shows the relation between reductions of HCl and SO_2 and relative humidity. Points in the figure are average values of the test points measured from the flue gas duct. Reduction is calculated from the measurements before and after the bag house filter.

As can be seen in the figures, reduction improves with increasing relative humidity. Results are more obvious to HCl than to SO_2.These findings are similar in the literature.

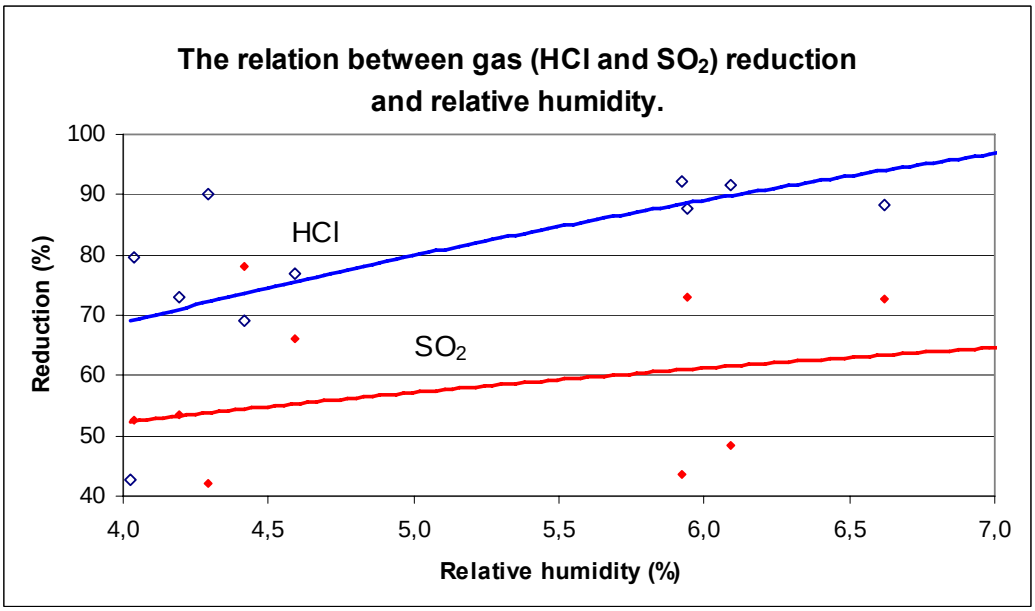

Figure 40: The relation between HCl and SO_2 reduction in the bag house filter and relative humidity during tests. These are average values from each test point.

6.1.2 The effect of flue gas absolute moisture

Figure 41 shows how fuel dryer affected flue gas absolute moisture in different temperatures. Values are divided based on fuel dryer (on/off) and temperatures (~ 140 °C and ~ 160 °C). Figure shows a clear relation between moisture and dryer. When dryer was off, moisture was ~ 20 vol-% and when it was on, values were ~ 25 vol-% in both temperatures.

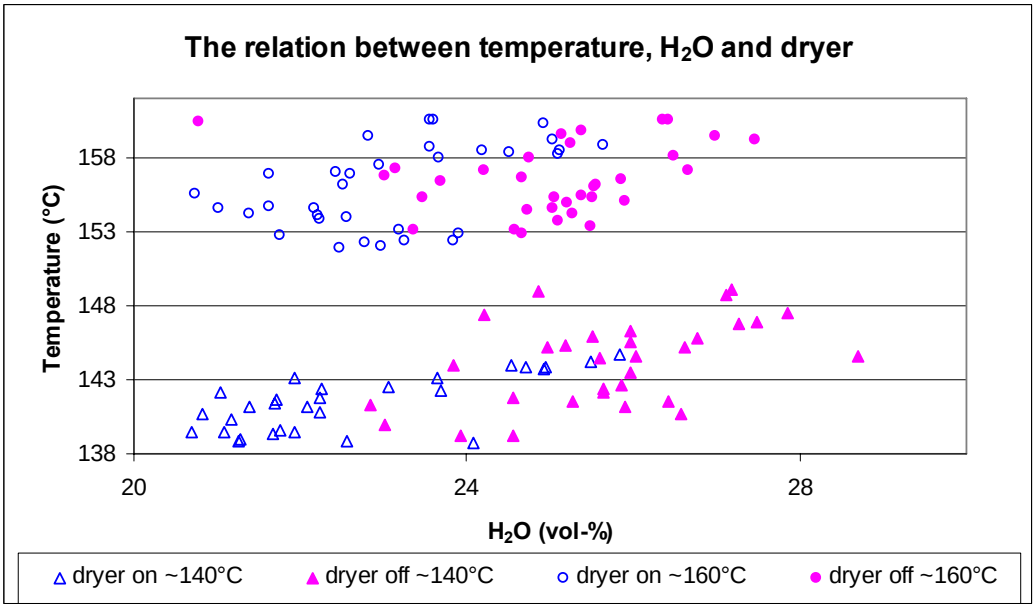

Figure 41: The effect of fuel dryer to absolute moisture in different temperatures. Values are averages (15 minute periods) during the whole test period.

Figure 42 shows the effect of dryer on HCl reduction as a function of flue gas absolute moisture. As seen in the figure, reduction does not seem to be affected solely with absolute moisture. Reduction is better in both cases with lower temperature. An exception is in test point 1. Different results can be because measurement was just started and there were some adjustment with FTIR.

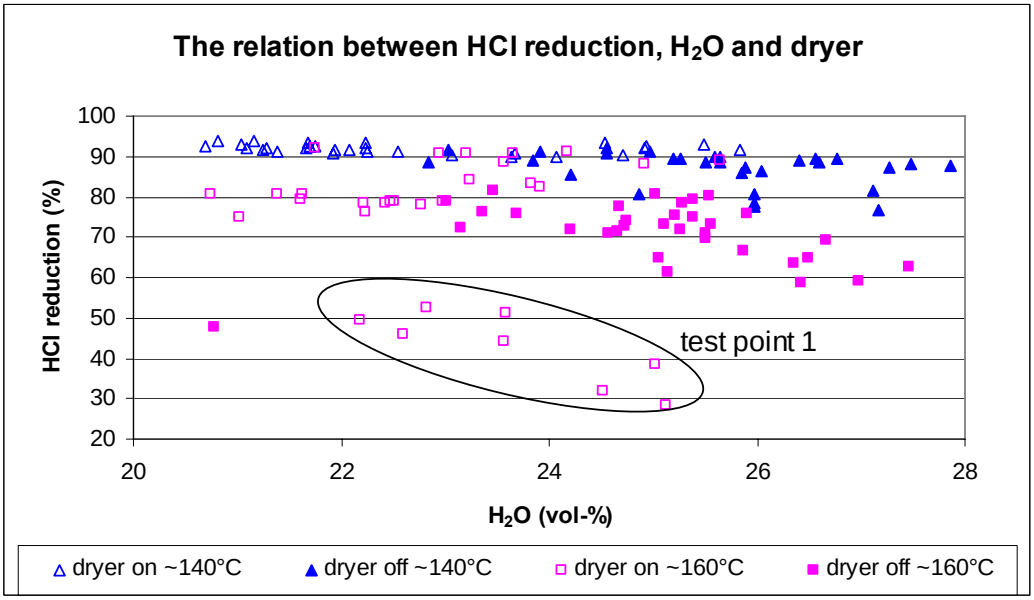

Figure 42: The effect of fuel dryer on HCl reduction in a function of absolute moisture. Results are in different temperatures. Values are averages (15 minute periods) during the whole test period.

Figure 43 shows the effect of dryer on SO_2 reduction. As seen in the figure, reduction is better when dryer is off and flue gas absolute moisture is higher. Same results are in both temperatures. Temperature does not seem to have effect. Temperature effect is studied more in chapter 6.3.

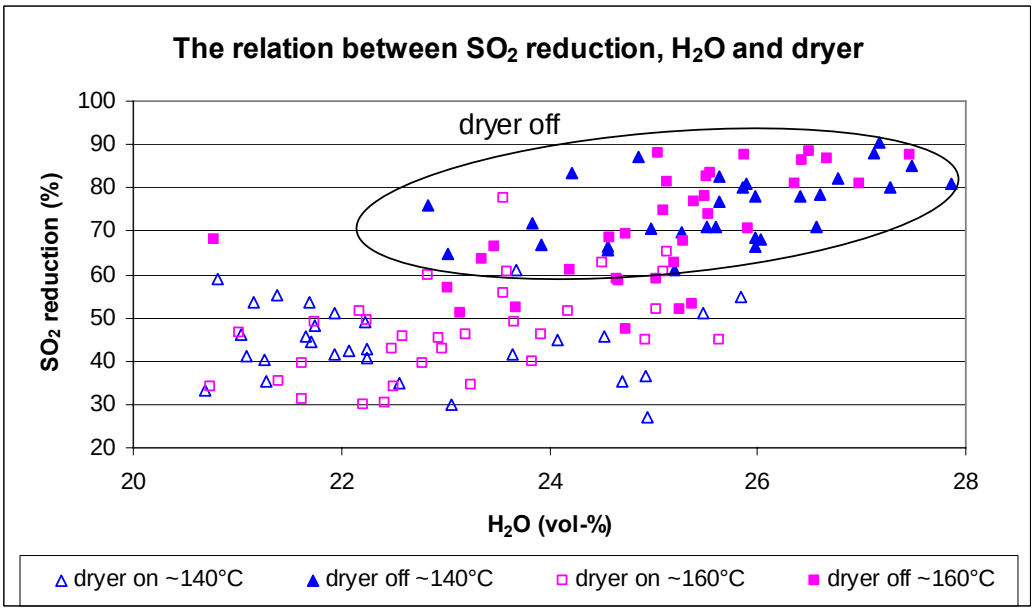

Figure 43: The effect of fuel dryer on SO_2 reduction as a function of absolute moisture. Results are in different temperatures. Values are averages (15 minute periods) during the whole test period.

6.2 The effect of absorbent

Figure 44 and Figure 45 show how limestone feed affects the reduction as a function of relative humidity. Points are divided into two groups based on temperature. It seems that limestone injection does not have effect on reduction of the gases. Many points without limestone were made with smaller load. This might have affected the results.

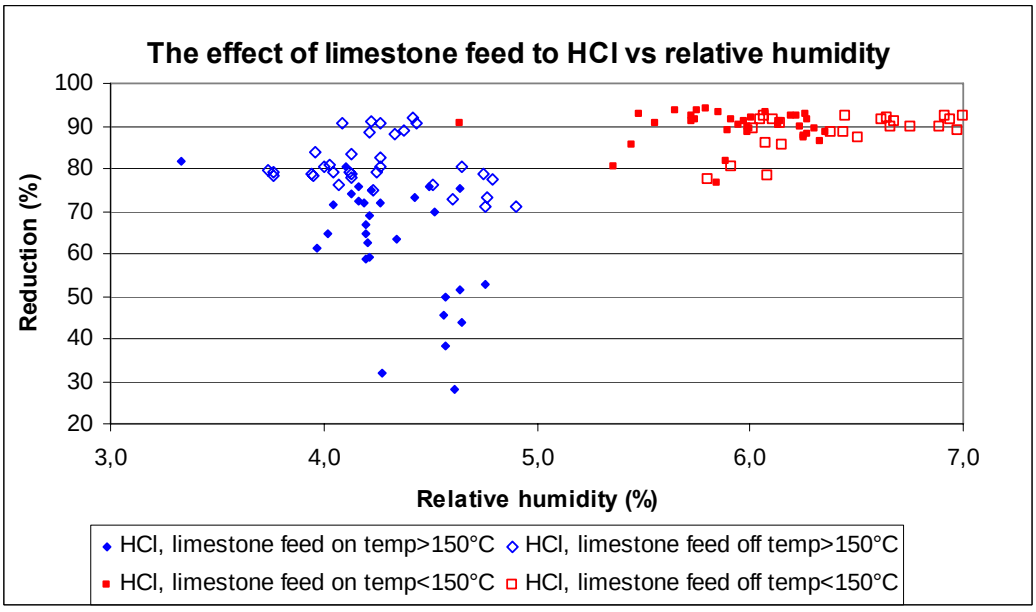

Figure 44: Reduction of HCl in tests with and without limestone feed. Reduction is a as function of relative humidity. Values are averages (15 minute periods) during the whole test period.

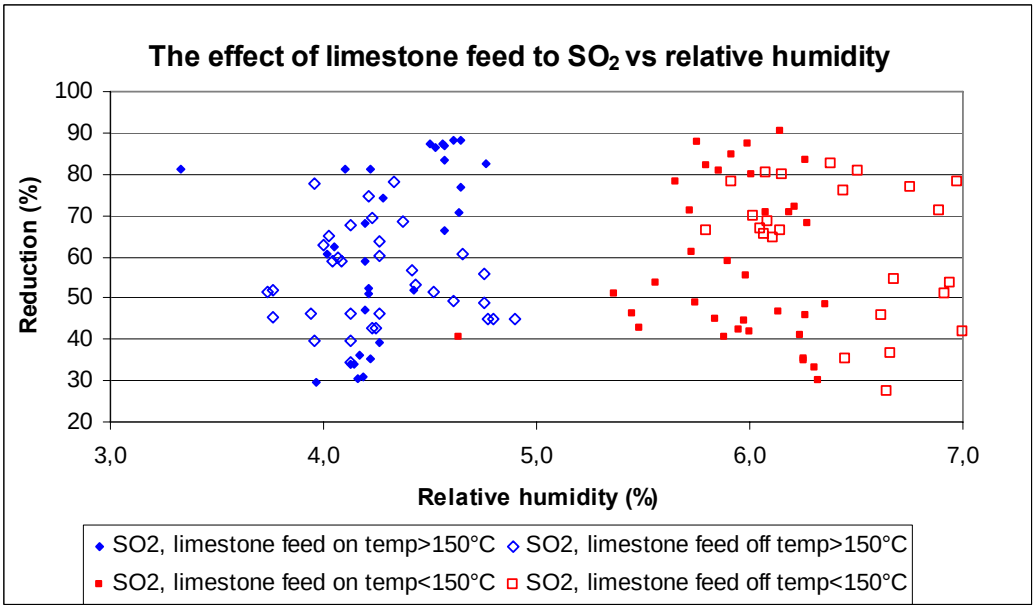

Figure 45: Reduction of SO_2 in tests with and without limestone feed. Reduction is a as function of relative humidity. Values are averages (15 minute periods) during the whole test period.

Figure 46 and Figure 47 show the same effect with and without limestone feed as a function of temperature. Based on the figures, it seems that limestone feed does not have effect on reduction of the gases. Higher temperature reduces reductions.

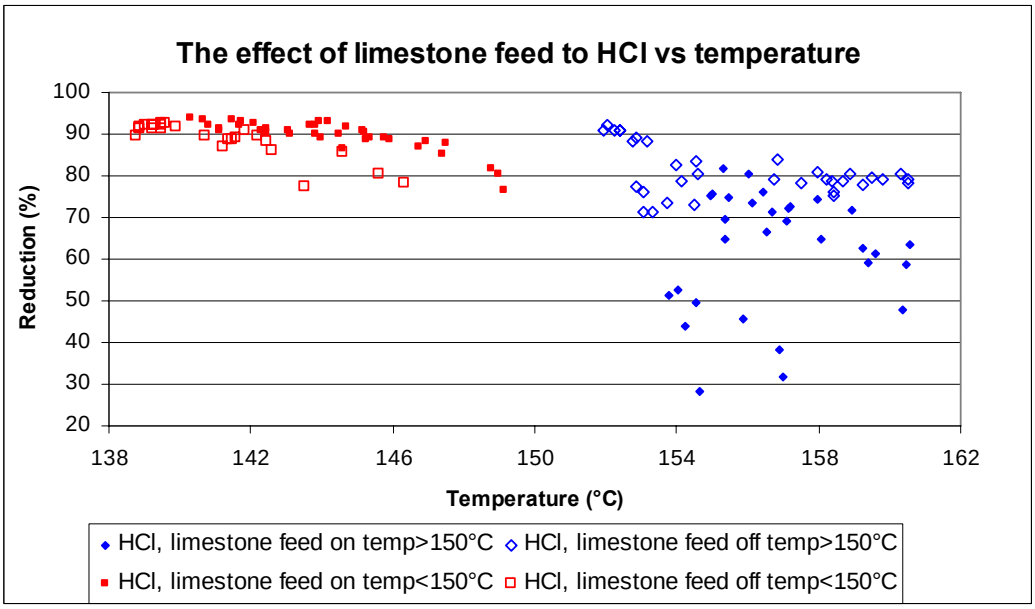

Figure 46: Reduction of HCl in tests with and without limestone feed. Reduction is a as function of temperature. Values are averages (15 minute periods) during the whole test period.

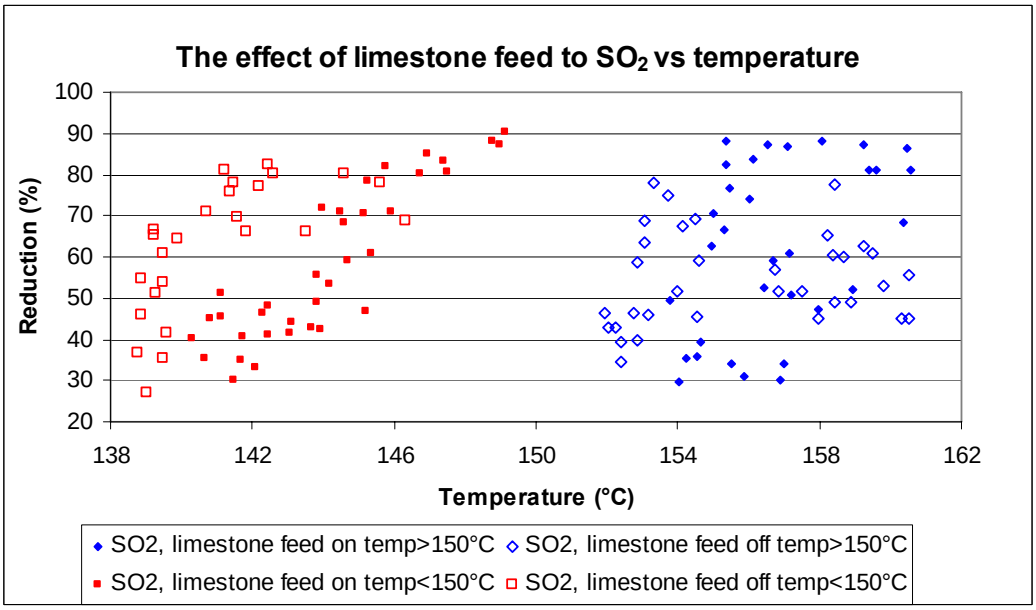

Figure 47: Reduction of SO_2 in tests with and without limestone feed. Reduction is a as function of temperature. Values are averages (15 minute periods) during the whole test period.

In Figure 48 and Figure 49, values are divided based on limestone feed, fuel dryer (on/off) and temperature (~ 140 °C and ~ 160 °C) to reduce other possible parameters that could affect.

According to the figures, limestone feed does not seem to have effect on reduction of HCl and SO_2. Parameter which has the most effect for HCl is temperature. Reduction with lower temperature is better. With SO_2, the parameter that has the most effect is fuel dryer. Reduction is better without the dryer.

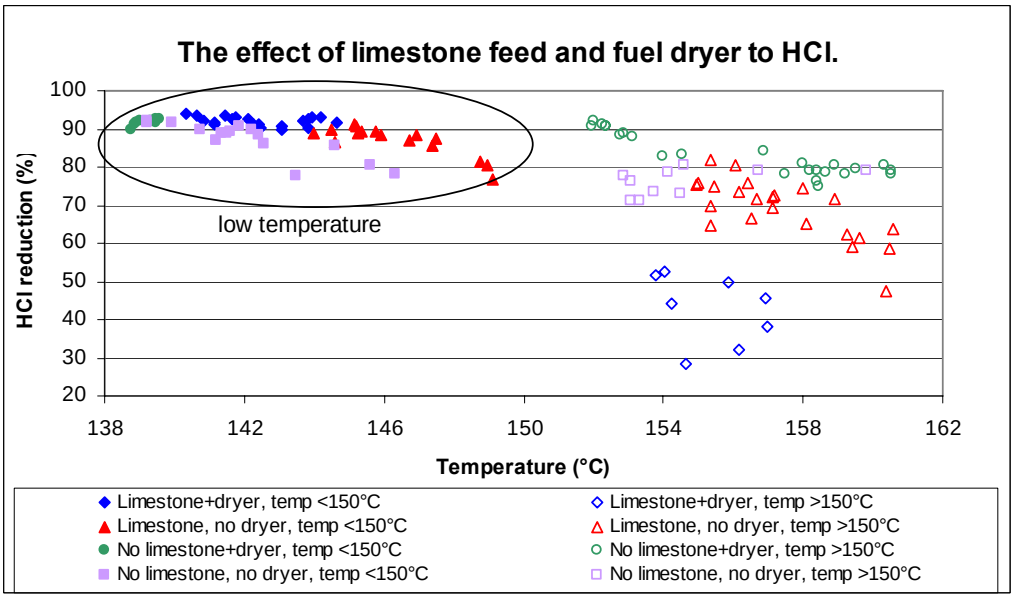

Figure 48: Reductions of HCl in tests with or without limestone feed and dryer on or off in different temperatures as a function of temperature. Values are averages (15 minute periods) during the whole test period.

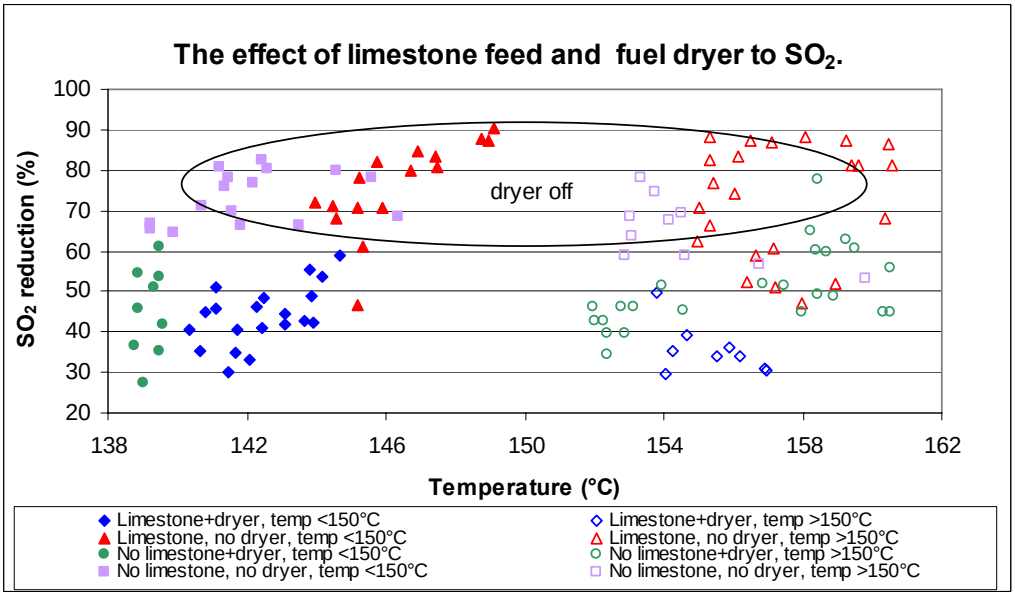

Figure 49: Reductions of SO_2 in tests with or without limestone feed and dryer on or off in different temperatures as a function of temperature. Values are averages (15 minute periods) during the whole test period.

6.3 The effect of temperature

Figure 50 shows the variation of temperature and absolute moisture during the tests. Temperature and moisture are measured in the flue gas duct before bag house filter. Temperature variation is between 139 °C and 161 °C and moisture variation between 16 vol-% and 29 vol-%.

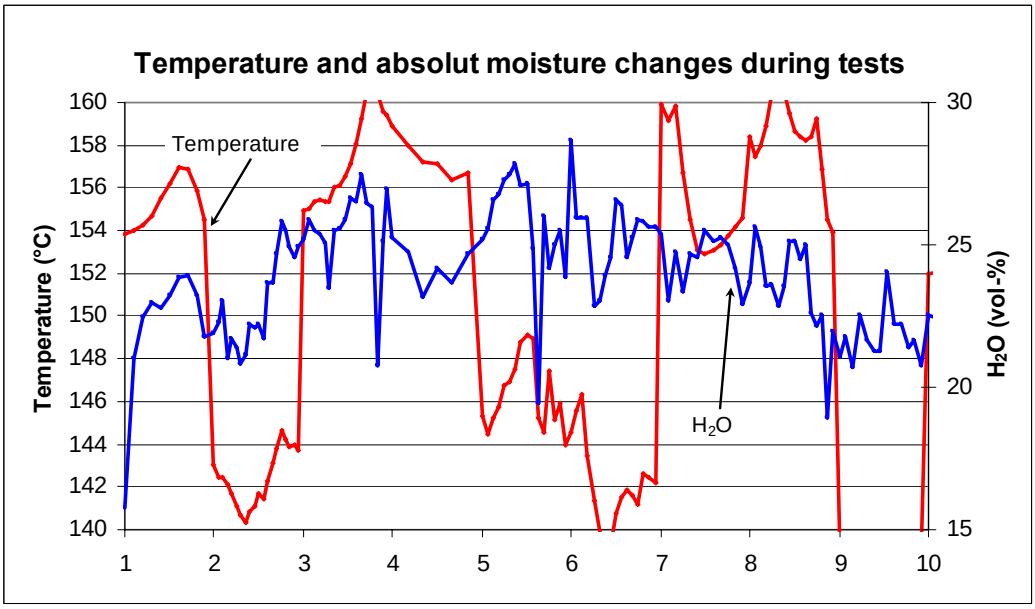

Figure 50: Temperature and moisture variation during the tests. Measurements are made before bag house filter. Values are averages (15 minute periods) during the whole test period.

Figure 51 shows how HCl and SO_2 reductions are related to temperature. Measurements were made from the flue gas duct. According to the figure, reduction of HCl seems to be decreasing with higher temperature. Temperature seems not to have effect on the reduction of SO_2.

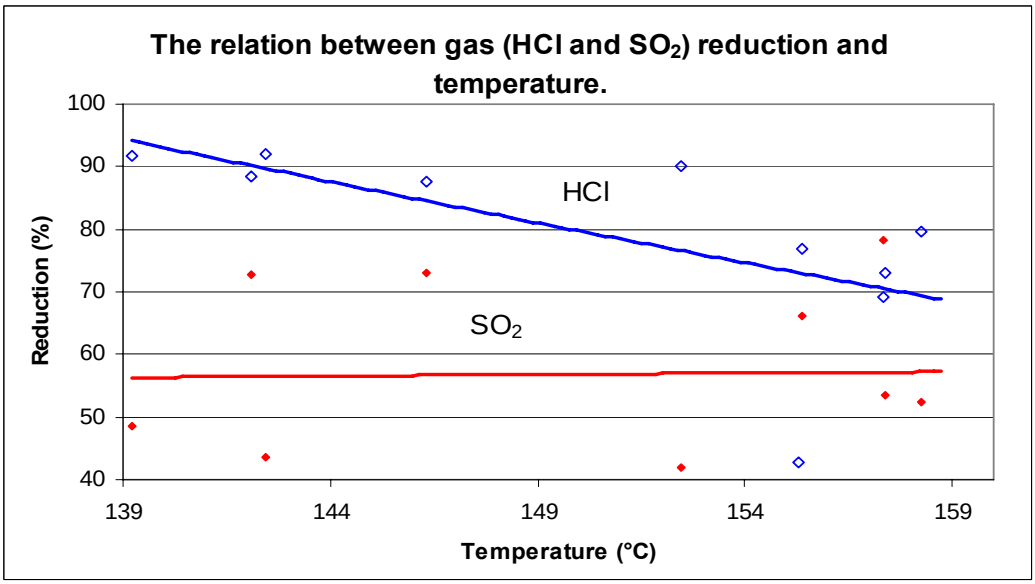

Figure 51: The relation between HCl and SO_2 reduction and temperature during tests. Temperature measurements were made before bag house filter. These are average values from each test point.

6.4 The effect of concentration changes

Figure 52 shows how different concentration of HCl affects reduction of HCl and same relation to SO_2. Gas concentrations were not changed intentionally, variation was because of the changes in the fuel mixture. Temperature measurement was made from the flue gas duct. As can be seen in the figures, reduction of HCl is better with higher concentrations.

Results for SO_2 seemed to be the opposite. According to literature, higher concentration of HCl leads to reduced reduction. It is because of plugging of the pores. Differing results may be because in the literature research, HCl was the only gas reacting with the limestone. Presence of SO_2 as well as other variables could affect the result.

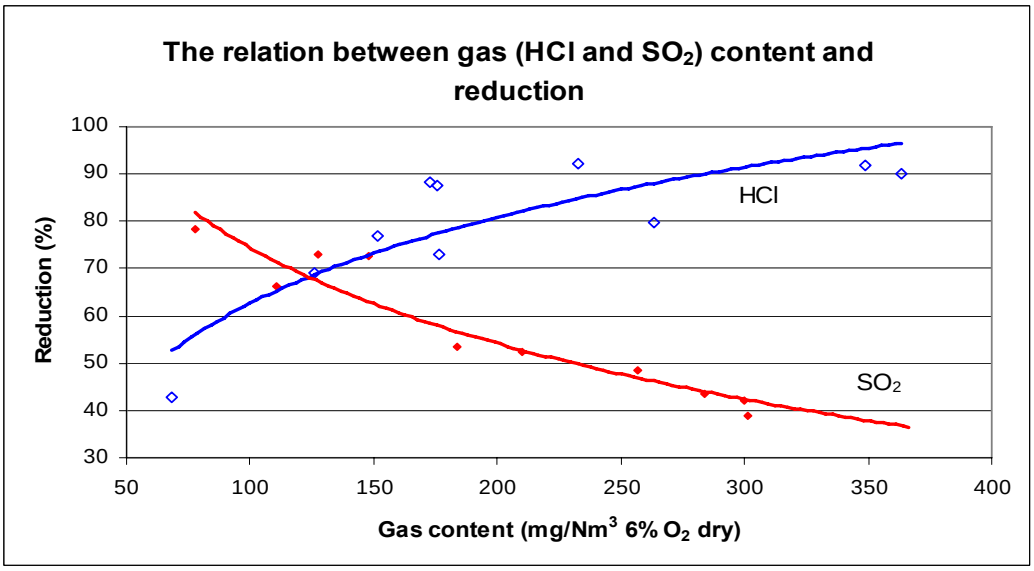

Figure 52: The relation between HCl and SO_2 amount and gas reduction. These are average values from each test point.

Figure 53 shows theoretical HCl contents without self reduction in the furnace, contents in the flue gas duct and in the stack in test points. In four of the points, theoretical values are lower than values in the duct. This suggests that there was not as much reduction in the furnace as expected. It can be also because of variation in the fuel. Fuel samples would have to be taken constantly to get more accurate results of the variation.

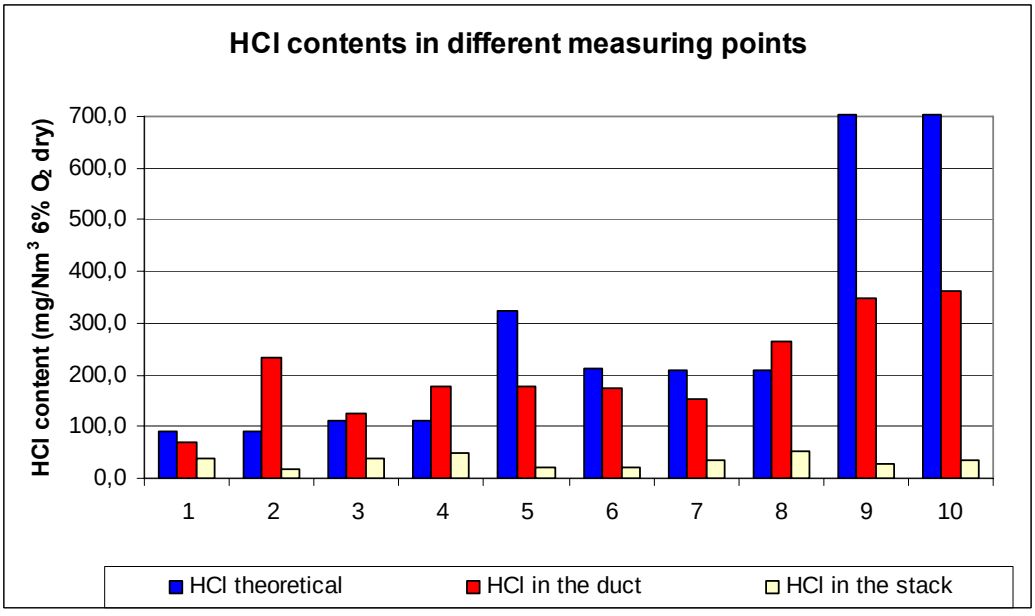

Figure 53: The contents of HCl in different measuring points. These are average values from each test point.

Figure 54 shows the same contents to SO_2. Theoretical values are clearly higher than values in the duct, which shows that good reductions have achieved already in the furnace. Fuel variation can also affect in these results.

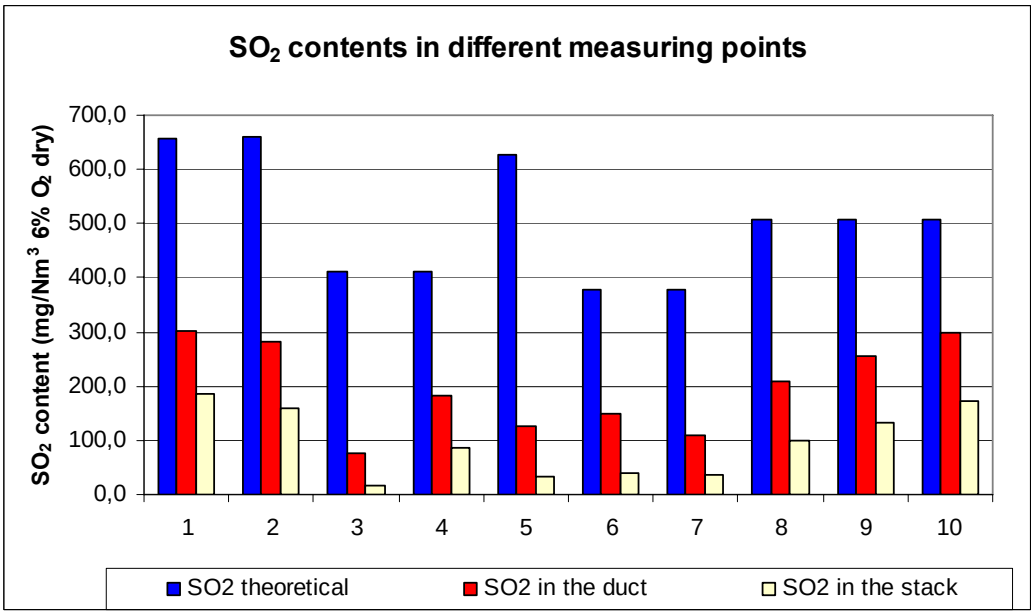

Figure 54: The contents of SO_2 in different measuring points. These are average values from each test point.

Figure 55 and Figure 56 show the percentage distribution of reduction for HCl and SO_2. According to the figure, HCl reduction in the furnace is small. Instead, the reduction in the bag house filter is good. It seems to be bigger than theoretical total reduction in many points.

Total reduction is the difference between theoretical values and measured values from the stack. Variation in the fuel as well as self reduction in the furnace affects the total reduction values, which is also seen in the figures above (Figure 53 and Figure 54).

For SO_2 reductions in the furnace are typically slightly better than in the bag house filter. Theoretical total reduction values are higher than reduction in the filter in every point.

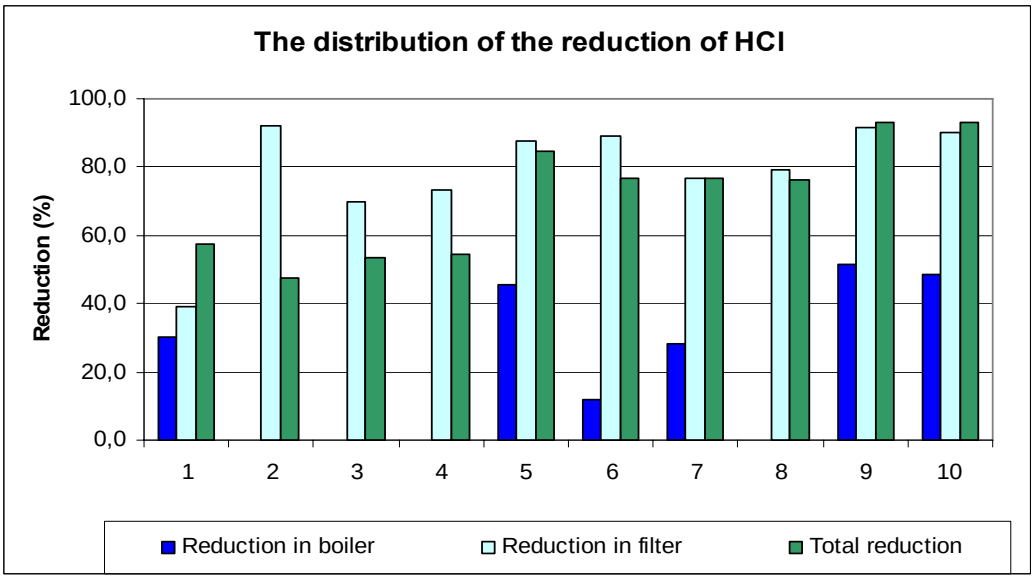

Figure 55: The relation between HCl amount and reduction in different measuring points. These are average values from each test point.

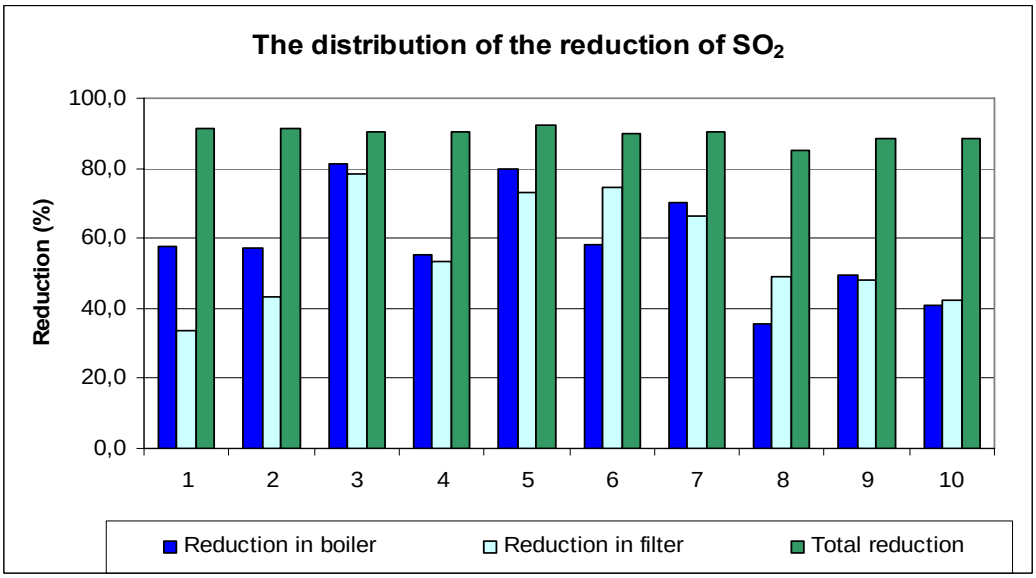

Figure 56: The relation between SO_2 amount and reduction in different measuring points. These are average values from each test point.

6.5 The effect of the relation between HCl and SO_2

Figure 57 shows how reductions of HCl and SO_2 are related to the HCl/SO_2 relation. Contents of the gases are mg/m^3 in 6 % dry O_2. Measurements are made from the flue gas duct. As seen in the figure, both reductions seem to be increasing when the relation increases.

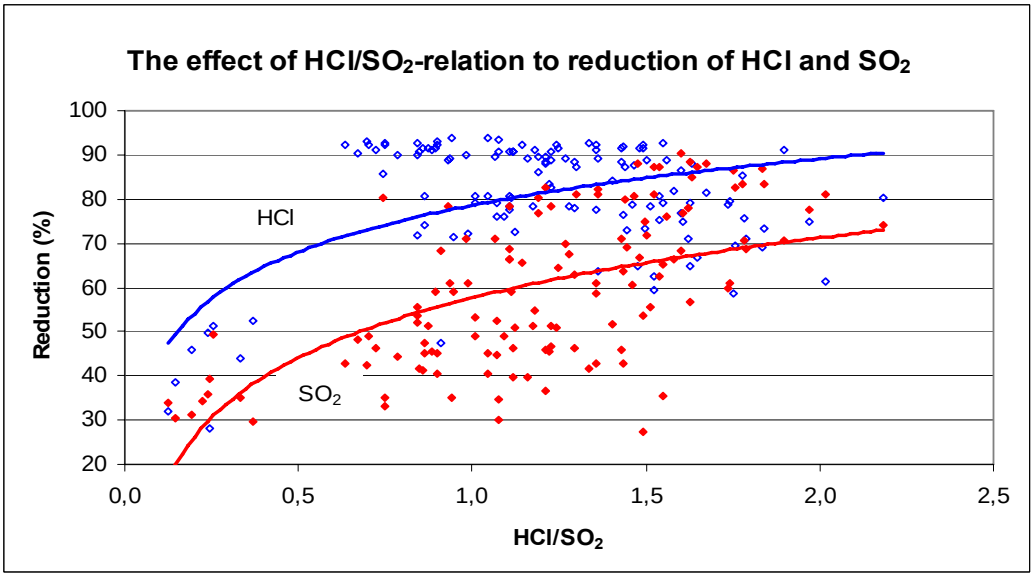

Figure 57: The reduction of HCl and SO_2 in the function of relation between the gases. Values are averages (15 minute periods) during the test period.

6.6 The effect of oxygen

The effect of oxygen in HCl and SO_2 reduction is in Figure 58. Tests were divided into two based on fuel load. That is because load difference could have affected the results. Measurements were made from the flue gas duct. Based on the figure, oxygen does not seem to have influence in the reduction of gases. According to literature, higher amount of oxygen should enhance the reduction of SO_2. The difference in the results can be because of some other parameter that affected the results. Oxygen contents were not intentionally altered in the measurement.

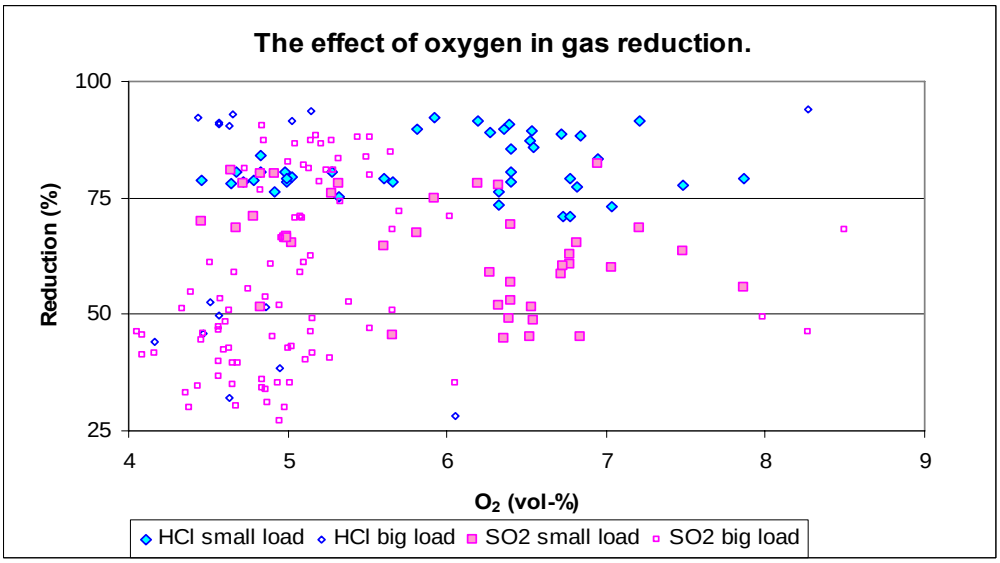

Figure 58: The effect of oxygen in reduction of HCl and SO_2. Tests are made with two fuel loads (30 kg/s and 20 kg/s). Oxygen is measured from the flue gas duct. Values are averages (15 minute periods) during the test period.

6.7 The effect of NO_x

Figure 59 shows how HCl and SO_2 reductions are related to NO_x concentration. NO_x measurements are made from the flue gas duct. HCl reduction and NO_x concentration do not seem to be related much. SO_2 reduction seems to be increasing with higher NO_x concentrations. Like with oxygen, results can be also because of some other parameter. NO_x values were not intentionally altered. Variation of NO_x is because of the variation in the fuel.

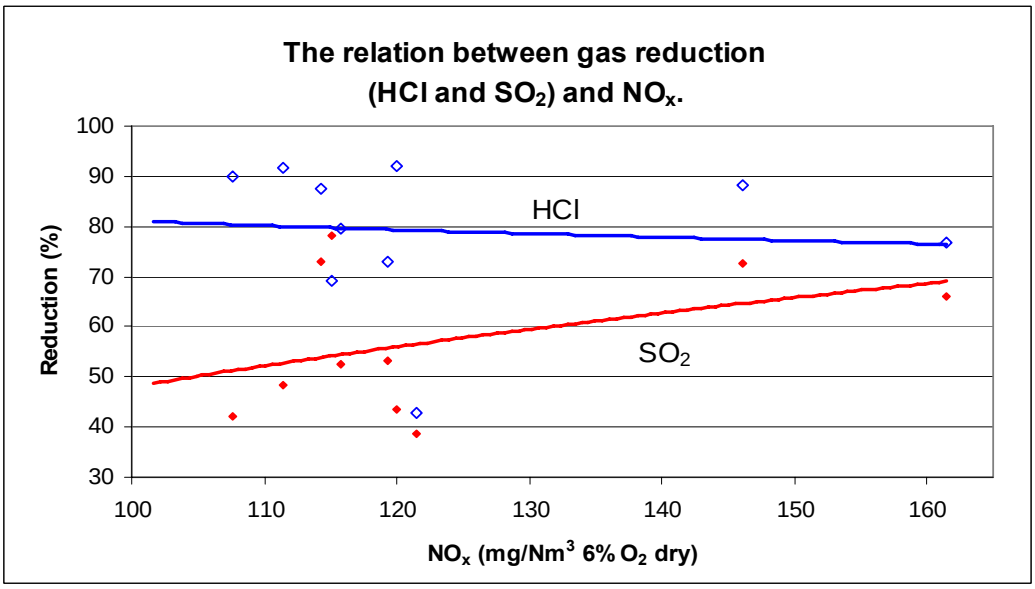

Figure 59: The relation between HCl and SO_2 reduction and NO_x. NO_x measurements are made from the flue gas duct. These are average values from each test point.

7. CONCLUSIONS

Findings that were discovered with literature research were the parameters that had effect on acid gas reductions. These were for independent absorption as well as simultaneous absorption of HCl and SO_2.

Most of the studies were about furnace injection and effect on temperature variation on this process. The effect of temperature variation on the injection of absorbent after the furnace was not found out properly in the literature research.

The purpose of the measurements was to find out how the findings in literature research could be made in full scale boiler circumstances. Lower emissions of acid gases were tried to achieve by chancing the process conditions according to the research.

There were so many parameters in the process, that it could not be sure how single variation in the process conditions affected. These can be studied in simulated studies, but it is not possible in full scale boiler.

Results of the measurements were (also in Figure 60 and in Figure 61):

- Increasing relative humidity increased reduction with both gases, especially with HCl
- SO_2 reduction was clearly better with higher flue gas absolute moisture, which indicates that reductions without fuel dryer were better
- Flue gas absolute moisture did not have a clear effect on HCl reduction
- HCl reduction was clearly better in lower temperatures
- Temperature effect on SO_2 reduction was not found out
- Higher HCl/SO_2 relation increased reduction for both gases
- Higher contents of HCl resulted in better reductions as with SO_2, the higher contents decreased reduction
- HCl reduction seemed to be better in the bag house filter than in the furnace
- SO_2 reduction was good already in the furnace and also in the bag house filter
- Total reductions of SO_2 seemed to be better than reductions of HCl
- Limestone injection did not have an effect in the reduction of HCl or SO_2, probably because of small injection amounts
- The effects of O_2 and NO_x was not found out

Results in the literature research and in measurements are mostly similar. The effect of limestone injection, temperature effects to SO_2 and the effects of oxygen and NO_x were different than in the literature. The lack of results with limestone feed can be explained with the small amounts of limestone that was injected. The effects of oxygen and NO_x might have not found out because of other changes in process conditions.

Based on these results there may be further measurements conducted later. Findings could be utilized and inconclusive results could be clarified.

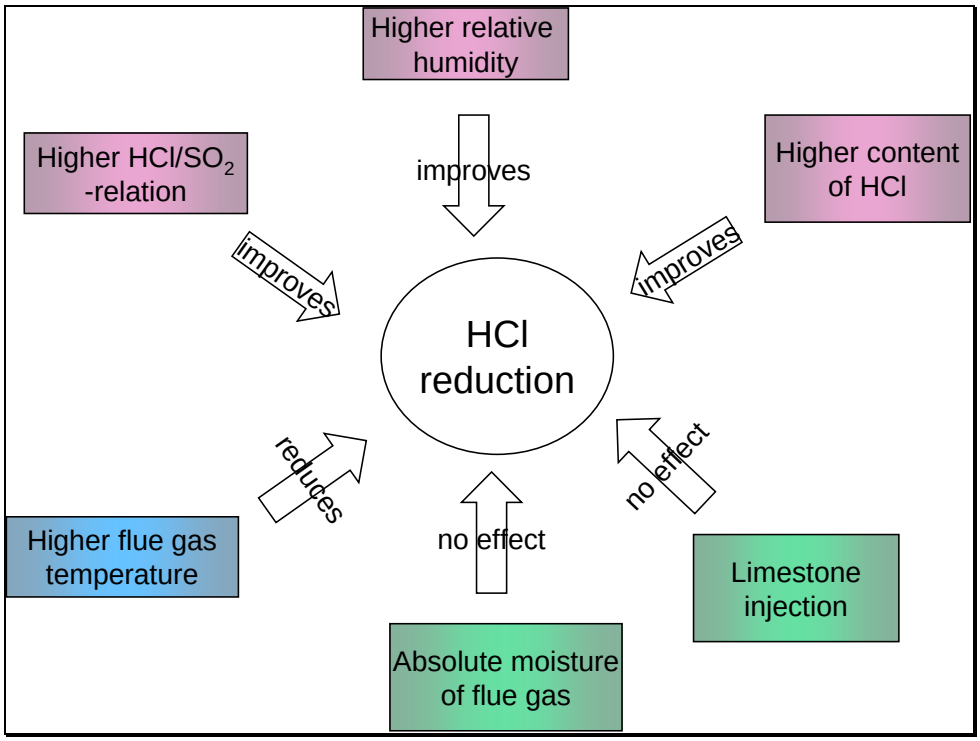

Figure 60: Parameters that affect HCl reduction.

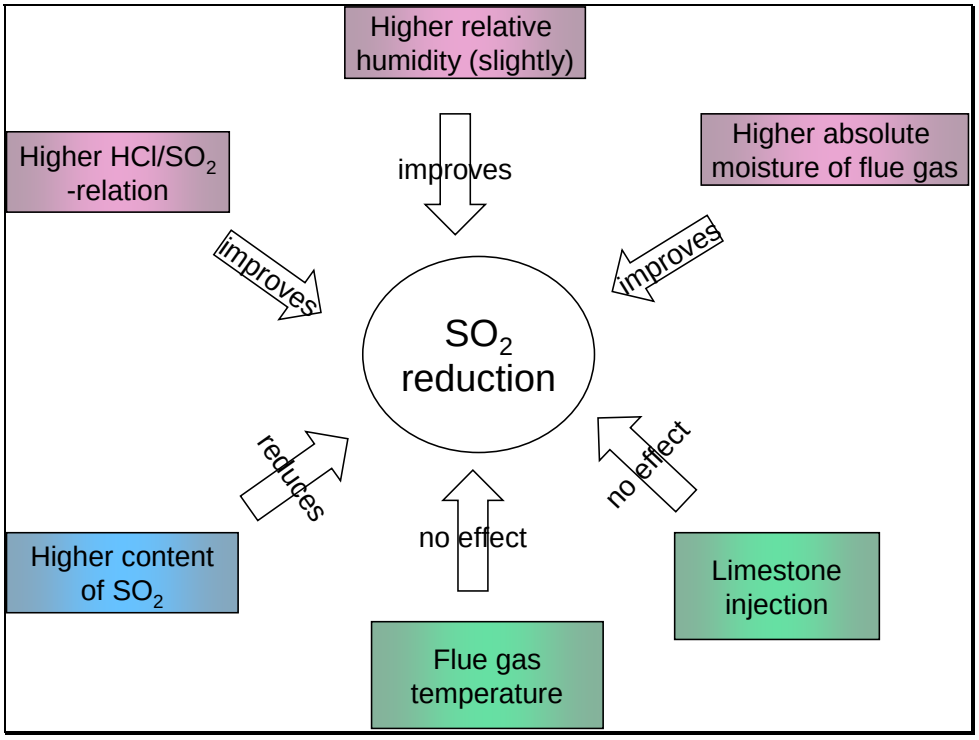

Figure 61: Parameters that affect SO_2 reduction.

REFERENCES

1. Wikström-Blomqvist, Evalena – Samuelsson, Jessica – Ohlsson, Anna. Optimerad rening av HCl och SO_2 med minskade kalktillsatser för torr rökgasrening. M6-635. Värmeforsk. Sverige. December 2006. 50s.
2. Krüger, Jörg. Development of the Semi-dry Flue Gas Cleaning at the Schwandorf Waste-to-energy Plant. VGB Power Tech 10/2007. 7s.
3. Partanen, Jatta – Backman, Peter – Bacman, Rainer – Hupa, Mikko. Absorption of HCl by limestone in hot flue gases. Part III: simultaneous absorption with SO_2. Fuel. September 2005. 10s.
4. Chrisholm, Paul N, – Rachelle, Gary T. Dry absorption of HCl and SO_2 with hydrated lime from humidified flue gas. Ind. Eng. Chem. Res. 38/1999. 12s.
5. Stein, Jens – Kind, Matthias – Schlünder, Ernst-Ulrich. The influence of HCl on SO_2 absorption in the spray dry scrubbing process. Chemical engineering journal 86/2002. 5s.
6. Matsukata, M. – Takeda, K. – Miyatani, T. – Uyeama, K. Simultaneous chlorination and sulphation of calcined limestone. Chemical engineering science 51/1996. 6s.
7. Lawrence, A.D. – Bu, J. The reactions between Ca-based solids and gases representative of those found in a fluidized-bed incinerator. Chemical engineering science 55/2000. 9s.
8. Hämälä, Sirpa – Laine, Jouko – Vesa, Paula. Ilmansuojelutekniikka. Tammertekniikka. Tampere 1992. 161s.
9. Lumme, Satu – Jalkanen, Katriina. Limestones in Sulphur Capture-report. Internal report by Kvaerner Power 2005. 53s.
10. Internal material by Metso Power
11. Technical specification of the test facility
12. http://www.wooster.edu/chemistry/analytical/ftir/default.html
13. http://en.wikipedia.org/wiki/Fourier_transform_spectroscopy
14. Raiko, Risto – Kurki-Suonio, Ilmari – Saastamoinen, Jaakko – Hupa, Mikko. Poltto ja palaminen. Teknillisten tieteiden akatemia. Jyväskylä 1995. 629 s.
15. Saanilahti, Sanna – Flue gas cleaning in cement industry. Internal report by Metso Power 2007. 32 s.

APPENDIX

Table 6: Constants A-E for calculation of relative humidity [14]

Compound	A	B	C	D*10^3	E*10^6	Temperature range (K)	%
Ar	24,018	-542,78	-8,4430	16,824	-	83,8–150,9	0,18
He	2,3826	-2,8323	4,1992	-506,18	38084,1	0,9–5,2	0,89
Ne	1,4691	-70,075	3,0607	-14,361	-	25,0–44,5	1,25
H_2	5,2366	-46,280	-0,44809	25,290	-	13,8–33,0	0,17
N_2	21,623	-455,57	-7,5107	17,214	-	63,2–126,4	0,16
O_2	5,6486	-411,30	1,8118	-25,042	62,612	54,1–154,8	0,36
CO	32,863	-606,91	-12,969	27,551	-	72,5–133,2	0,37
CO_2	47,544	-1792,2	-16,559	13,833	-	217,2–304,4	0,12
H_2O	16,373	-2818,6	-1,6908	-5,7546	4,0073	273,2–647,4	0,09
H_2O_2	44,791	-4022,7	-13,076	4,5627	-	273,1–728,2	2,44
SO_2	46,554	-2456,3	-15,169	9,0026	-	205,6–430,8	0,70
SO_3	160,89	-8081,2	-54,240	4,3154	17,432	272,2–491,5	0,55
N_2O	54,061	-1894,7	-19,406	16,572	-	184,7–309,7	0,62
NO	258,32	-4361,0	-115,06	167,15	-	116,4–270,3	0,69
NO_2	33,024	-2276,7	-10,143	8,9510	-	261,9–431,6	0,26
NH_3	38,440	-2066,2	-12,105	7,7768	-	208,2–405,6	0,20
N_2H_4	60,878	-3880,3	-20,575	15,585	-5,0525	288,2–653,2	1,50
HF	66,244	-2588,0	-25,140	28,493	-9,9602	198,5–461,2	0,44
HCl	136,05	-3047,3	-58,416	95,496	-58,507	122,4–324,7	0,47
HBr	-351,11	5375,2	161,89	-259,04	157,16	190,2–363,2	0,97
HI	33,943	-1777,9	-10,620	6,9457	-	213,7–424,2	0,52
CH_4	22,573	-656,24	-7,3942	11,896	-	91,0–191,3	0,45
C_2H_6	16,316	-1074,8	-3,1434	4,5534	10,373	93,7–305,5	0,42
C_3H_8	36,007	-1737,2	-11,666	8,5187	-	144,3–370,0	0,46
C_2H_4	30,895	-1196,8	-10,153	9,9351	-	104,2–283,3	0,80
C_3H_6	36,877	-1725,5	-12,057	8,9948	-	123,2–365,3	0,58
C_4H_8	41,610	-2158,8	-13,580	8,6536	-	143,2–419,5	0,68
C_6H_6	51,204	-3245,7	-16,403	7,540	-	280,8–562,6	0,65
$C_{10}H_8$	192,16	-8336,3	-72,834	56,768	-17,319	356,1–748,2	0,94
CH_3OH	-42,629	-1186,2	23,279	-35,082	17,578	205,8–513,2	0,99
C_2H_5OH	-10,967	-2212,6	10,298	-21,061	10,748	228,2–516,2	0,96
C_3H_7OH	-338,31	5127,5	148,80	-175,79	74,666	273,2–536,9	1,18
C_4H_9OH	-458,03	7760,4	199,14	-229,44	95,289	272,0–563,0	1,19